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LESSONS
ON
THERMODYNAMICS.

BY
ROBERT E. BAYNES, M.A.

SENIOR STUDENT OF CHRIST CHURCH, OXFORD
AND LEE'S READER IN PHYSICS

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P R E F A C E.

THE substance of the following Lessons formed a course of Lectures on Thermodynamics which were delivered at the Clarendon Laboratory, Oxford, in Hilary Term 1876. They have been revised, and are now published in the hope of supplying a complete English Mathematical Introduction to the Dynamical Theory of Heat. No such treatise exists at present: Professor Rankine's *Manual of the Steam-Engine and other Prime Movers*, being written for the use chiefly of practical Engineers, contains only a short sketch of the subject; Professor Tait's *Thermodynamics* gives very valuable information as to the history of the theory and its place in the general Science of Energy, but is too brief for the wants of the student; and Professor Clerk Maxwell in his *Theory of Heat* has not gone far into the Mathematical Development, though in other respects the work is most valuable and perhaps the most suggestive that has been written on the subject. To this last book the present writer owes his first knowledge of Thermodynamics, and takes this opportunity of acknowledging his great obligations to it.

Many original memoirs have been studied in the course of the preparation of these Lessons, and copious reference is made to them: the student will thus be able to find more extended investigation of many particular points of the theory. Dr. Zeuner's *Grundzüge der mechanischen Wärmetheorie*, M. Verdet's *Théorie Mécanique de la Chaleur*, and M. Saint-Robert's *Principes de Thermodynamique* have also been consulted.

No account is given of the kinetic theory of gases, because Mr. Watson's treatise *The Kinetic Theory of Gases* contains all that is required. The student will also find an elementary and lucid explanation in Professor Clerk Maxwell's *Theory of Heat*, Chapter XXII.

CHRIST CHURCH,
May, 1878.

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EXPLANATION OF REFERENCES.

<i>Pogg. Ann.</i>	= Poggendorff's Annalen.
<i>C. R.</i>	= Comptes rendus de l'Académie des Sciences.
<i>B. A. Rep.</i>	= British Association Report.
<i>Phil. Trans.</i>	= Philosophical Transactions of the Royal Society.
<i>Trans. R. S. E.</i>	= Transactions of the Royal Society of Edinburgh.
<i>Phil. Mag.</i>	= Philosophical Magazine.
<i>Proc. R. S.</i>	= Proceedings of the Royal Society.

The number in the square brackets [] is the *series*, that in Roman characters the *volumes*, that in ordinary brackets () the *year*, and the final number is the *page*.

ERRATA.

p. 23, line 15, for 41-675	read 41-55.
„ „ „ 20, „ or suggestive a letter „	with our notation.
„ 77, „ 14, „ <i>ldv</i>	„ <i>ldv</i> .

In Fig. 19, page 67, a dotted curve should be drawn through *C* less inclined to *Ov* than either of the other curves.

LESSONS ON THERMODYNAMICS.

ERRATA AND CORRIGEND.

- Page 8, line 2. *For* force *read* action
- „ —, „ 4. *For* upon *read* per
- „ 15, „ 16. *Add* the envelope being usually of glass
- „ —, „ 24. *Add* per square centimetre
- „ 17, „ 29. *For* conductivity *read* conductivity
- „ 18, „ 33. *Delete* per unit area
- „ 19, „ 13. *For* on the axis, . . . minimum *read* by a line on the pv -plane that does not pass through the origin, since the volume cannot be reduced to nothing
- „ 23, „ 15. *For* 41·675 *read* 41·55
- „ —, „ 20. *For* or suggestive a letter *read* with our notation
- „ 25, „ 15. *For* has . . . as *read* is no heavier when hot than
- „ —, „ 17. *Delete* in nitrogen or
- „ 28, „ 12. In the experiment described the ends of the wire were connected *inside* the tube, the commutating arrangement being used only in proving that the heat generated is proportional to the square of the current-intensity
- „ 34, „ 33. *After* plate *insert* bent at the bottom so as to form a narrow ledge
- „ —, „ 36. *Before* between *add* on the ledge
- „ 35, fig. 6. Remove the rest and bend round the iron plate attached to B so as to support C
- „ —, line 34. *After* cooling *add* per degree of this excess
- „ 40, „ 1. *For* a state *read* all states
- „ —, „ 36. *After* conduction *add* friction
- „ 42, „ 25. *Delete* per unit area
- „ 43, „ 19. *For* similarly *read* therefore
- „ —, „ 22. *Add* These lines are also called *isopleths*
- „ 44, „ 4. *Add* we shall however retain both terms, since the former not only denotes the latter but includes also the further notion of entropy being a measurable quantity
- „ —, „ 31. *Add* On a diagram with volume and entropy as coordinates no thermal lines of the same type intersect each other

- Page 45, line 18. *For shews read points out*
- " 50, " 8. *After large add in comparison with the volume of the working substance*
- " 63, " 3. *For the exponent T read T'*
- " —, " 8. *Delete we . . . again on line 18*
- " —, " 21. *Delete they . . . cold on line 23*
- " 67, " 1. *Before lines insert real thermal*
- " —, " 4. *For also read necessarily*
- " —, fig. 19. *Draw a dotted curve through C less inclined to Ov than either of the other curves*
- " 68, line 34. *For $OB'CO'$ read $O'B'CO'$*
- " 76, " 22. *For cycles read processes*
- " —, " 24. *For cycle read process*
- " 77, " 14. *For ldv read $l\delta v$*
- " 78, " 4. *For $\frac{\partial E}{\partial p}$ and $\frac{\partial E}{\partial v}$ read $\left(\frac{\partial E}{\partial p}\right)_v$ and $\left(\frac{\partial E}{\partial v}\right)_p$*
- " —, " 6. *For $\frac{\partial v}{\partial p}$ and $\frac{\partial p}{\partial v}$ read $\left(\frac{\partial v}{\partial p}\right)_v$ and $\left(\frac{\partial p}{\partial v}\right)_p$*
- " —, " 11. *For $\frac{p}{v}$ read $\frac{p}{\tau}$*
- " 83, " 31. *For 25 read 24*
- " 85, " 14. } *For $\frac{\partial K}{\partial p} - \frac{\partial L}{\partial t}$ read $\left(\frac{\partial K}{\partial p}\right)_t - \left(\frac{\partial L}{\partial t}\right)_p$*
- " 86, " 12. }
- " 85, " 15. } *For $\frac{\partial v}{\partial p} - \frac{\partial p}{\partial v}$ read $\left(\frac{\partial v}{\partial p}\right)_v - \left(\frac{\partial p}{\partial v}\right)_p$*
- " 86, " 14. }
- " —, " 13. *For $\frac{\partial K}{\partial p}$ read $\left(\frac{\partial K}{\partial p}\right)_t$*
- " 87, " 7. *For these equations read this equation*
- " 90, " 13. *After expression add (in terms of v and t)*
- " 92, " 15. *Add In this case $dS = (k - t\mathfrak{E})dt$*
- " —, " 24. *For 28 read 33*
- " 96, eq. (44). *For $\frac{\partial w}{\partial x}, \frac{\partial w}{\partial y}$ read $\frac{\partial W}{\partial x}, \frac{\partial W}{\partial y}$*
- " 97, eq. (50). *Multiply the second determinant by t^2*
- " 98, table. *The expression in the 2nd row 19th column should be*

$$K \frac{\partial t}{\partial v} - p;$$

that in 4th row 4th column, $-\frac{\partial t}{\partial v};$

that in 5th row 5th column, $-\frac{K}{kp} \frac{\partial p}{\partial v};$

- that in 5th row 13th column, $\frac{t}{kp} \frac{\partial p}{\partial t}$;
 that in 5th row 18th column, $-\frac{kp}{K} \frac{\partial v}{\partial p}$;
 that in 5th row 20th column, $\frac{kp}{t} \frac{\partial t}{\partial p}$;
 that in 6th row 4th column, $\frac{t}{kp} \left(K \frac{\partial p}{\partial v} + p \frac{\partial p}{\partial t} \right)$;
 that in 6th row 12th column, $\frac{t}{kp} \left(p - t \frac{\partial p}{\partial t} \right)$;
 that in 6th row 14th column, $\frac{kp}{t \left(K \frac{\partial p}{\partial v} + p \frac{\partial p}{\partial t} \right)}$;
 that in 6th row 16th column, $\frac{kp}{t \left(p - t \frac{\partial p}{\partial t} \right)}$.

Page 100, line 2. For k read k'

„ —, „ 8. Add and $k' = k - t'v$, t' being equal to \mathfrak{U}

„ 101, „ 2. For 25 read 24

„ 102, „ 23. For megadynes read atmospheres, or else add per square centimetre

„ 104, „ 1. For the temperature read temperature

„ —, „ 2. After body add i.e. is a function of this particular temperature

„ 105, „ 10. For conductibility read conductivity

„ 106, „ 15. After T add i.e. a function of T

„ 107, „ 24, 29. For atoms read molecules

„ —, „ 28. For $na\bar{k}$ and $a\bar{k}$ read $n\mu\bar{k}$ and $\mu\bar{k}$

„ —, „ 29. For a read μ

„ —, „ 30. For atomic weight read molecular mass

„ 108, „ 10. For weight read mass a

„ —, „ —. After unity add so that its molecular mass μ is two

„ —, „ 12. For $a\bar{k} = 100$ read $\mu\bar{k} = 200$

„ —, „ 29. For 100 read 200, and for $\Sigma.n$ read $\Sigma \frac{n}{m}$

„ —, „ 31. For weight read mass, and add and whose molecule consists of m atoms

„ 110, „ 3. After its insert extreme

„ —, „ 17. Add Sir W. Thomson calls it the thermodynamic motivity of the body

„ 112, „ 11. For $\frac{t_0}{T-t_0} \log_e \frac{T}{t}$ read $\frac{t_0}{T-t_0} \log_e \frac{T}{t_0}$

„ 113, „ 8. After energy insert or thermodynamic motivity

- „ 115, „ 23. For the work to bottom of page substitute while the maximum work obtainable by cyclical processes from heat-energy $\int dH$ taken in by a body along a given path is, by (1), less than $\int dH$ by $t_0 \int \frac{dH}{t}$, where t_0 is the lowest available temperature, the maximum work that can be done in a cycle partly formed of this path as a whole is less than $\int dH$ by $t_0(\phi - \phi_0)$, where ϕ, ϕ_0 are the entropy of the body in the final and initial states defined by this path, so that an amount

$$t_0 \left(\phi - \phi_0 - \int \frac{dH}{t} \right)$$

of available energy is lost owing to the nature of the path, or this amount of energy is dissipated along the path. This expression, by (20), § 51, is always positive when the process is non-reversible, being zero for reversible processes.

If the process is cyclical, the dissipation is $-t_0 \int \frac{dH}{t}$.

- Page 111, line 17. For T_0 read τ_0
- „ 122, „ 10. For the air read in the water
- „ —, „ 30, 31. For 0.02 read 0.2
- „ 129, „ 6. Before and insert so that the equation $p v = R \tau$ cannot be taken to hold for air, as M. Regnault has otherwise shewn
- „ 140, „ 12. For volume read temperature
- „ 141, eq. (17). For u_1, u_2 read v_1, v_2
- „ 148, line 21. For c. a. s. read our
- „ 156, „ 14. After lose insert on each side
- „ 163, „ 11. For fraction read function
- „ 165, „ 6. Delete ° and substitute degree
- „ —, „ 32. See however *Nature*, xxiii. (1880) 211 (Rep. Chem. Soc.).
- „ 169, „ 20. For log read \log_0
- „ 186, „ last. For $\phi +$ read $\phi -$
- „ 187, „ 28. For 0.0074 read 0.00734
- „ 191, „ 13. For liquids read fluids
- „ 199, „ 32. For A . . . figure substitute Two receivers are required for this engine, one coupled directly without any valves to each end of the cylinder, and the plunger of one is always half a stroke before that of the other
- „ 203, „ 9. Add This engine is not perfect because condition (1) of § 106 is not satisfied; for maximum efficiency, either AB must be an adiabatic as well as CD , or CD must be is-adiabatic with AB and not an adiabatic
- „ 204, „ 17. For lowers and increases read lower and increase

CHAPTER I.

Introductory Mechanical Principles.

1. Fundamental Units. In Mechanics it is necessary to employ units for the expression of the different measurable quantities that come under consideration: all these may however be derived from the three simple units of Length, Mass, and Time. We shall in this chapter briefly describe such of these mechanical quantities as concern us at present, employing the Centimetre-Gram-Second or c.g.s. system of units, for an exhaustive treatment of which the student is referred to Professor Everett's *Illustrations of the Centimetre-Gramme-Second System of Units* (1875).

Length. The unit of length is one centimetre: it is the hundredth part of the length of a certain platinum bar at Paris, called the *Mètre*, when at the temperature of melting ice. Captain Clarke¹ finds that 1 c. is 0.3937043196 inch, so that the British foot contains 30.47972654 c.

Mass. The unit of mass is one gram: this is the thousandth part of the mass of a certain piece of platinum, called the *Kilogramme des Archives*, which is kept in Paris. Professor Miller² has determined 1 g. to be 15.43234874 grains, so that a British pound is 453.59265254 g. He also concludes³ from Professor Kupffer's comparison of standards that the mass of 1 c.c. of water of maximum density (*i.e.* at 4°C.) is 1.000013 g. and not 1 g. exactly.

Time. The unit of time is one solar second, and the most recent discussions⁴ give

$$365.24222 \times 24 \times 60 \times 60 \text{ or } 31556928 \text{ seconds}$$

¹ *Proc. R. S.* xv. (1866) 313.

² *Phil. Trans.* cxlvi. (1856) 890.

³ *Proc. R. S.* xiv. (1865) 293, note.

⁴ *Main's Astronomy* (1863), 99.

as the length of the tropical year, that is, the time which elapses between two successive transits of the sun through the vernal equinox. It is to be feared that this interval is not absolutely constant; so slowly however is it lengthened, that observation through many hundred years can scarcely detect the change.

Velocity. The unit of velocity is one centimetre per second.

Acceleration. The unit of acceleration is one centimetre per second per second.

2. Force. Force is that which produces motion in a body, and the unit of force is that force which acting on unit mass for unit time produces in it unit velocity. In the c. g. s. system it is called a *dyne*: a million dynes, which for us is a more convenient unit, we shall term a *megadyne*.

Forces are usually measured by weights, that is, by the earth's attraction upon masses; they are then comparable only at the same spot, as the attraction varies with the position on the earth's surface. This is called the *gravitation* measure of force: it is reduced to absolute measure on multiplication with g , which denotes the number of units of acceleration impressed on a falling body at this spot by gravitation; for the weight of a mass acting on the mass for one second generates in it, if allowed freely to fall, a velocity of g centimetres per second, or the weight of a gram at this place is g dynes. The value of g should be determined by pendulum or other experiments at each different spot: it is well given however by the formula¹

$$g = 978.048 (1 + 0.00514491 \sin^2 \lambda) \left(1 - \frac{5h}{4r}\right),$$

where λ is the latitude, h the height above sea-level, r the earth's mean radius (about² 636669500 c.). The form of this formula is given by theory, and its constants are deduced from many combined observations: it may be written

$$g = 980.564 - 2.516 \cos 2\lambda - 0.000002 h,$$

which is more convenient for calculation. Thus at Oxford

¹ *Mem. R. A. S.* vii. (1833) 94, and Pratt's *Figure of the Earth* (1871), 51.

² Clark's *Earth (Figure of the)*, in the *Ency. Brit.* vii.

(lat. $51^{\circ} 45' 36''$ N.) the weight of a gram is 981.15 dynes, and at Manchester (lat. $53^{\circ} 29'$ N.) it is 981.30 dynes.

Much confusion is introduced into ordinary language by the loose way in which such terms as gram and pound are used, not only as masses or quantities of matter (which is their real signification), but also as the weights of these masses, that is, as forces. This must be avoided: the *force of a pound* means absolutely nothing at all, and should never be used, while the *force of a pound's weight* or the *force equal to the weight of a pound* is perfectly intelligible; and these latter forms of expression, even though the longer, must always be employed. This error has arisen from the conception of mass being more difficult than the conception of weight, which is proportional to it, and from the fact that masses are usually compared by the balance, in which the weight of one mass is made to equilibrate the weight of another. The *weights* of a balance are of course not real weights or forces, but masses whose weight is put against that of the bodies weighed.

3. Work. The unit of work is that work which is done when unit force is overcome through unit distance: this on the c.g.s. system is called an *erg*. We shall however find that in thermodynamics a million ergs is a more convenient unit, and this we shall call a *megale*rg. Work may be done in communicating motion to a body as well as in overcoming force; this aspect of work will be exhibited in the next article.

The practical unit of work used by engineers is a gravitation measure: in British units it is a foot-pound, or the work done against the earth's attraction in raising one pound through the height of one foot, and is equal to 13825.38 g ergs; in metrical units it is a kilogrammetre, or the work required to raise one kilogram through one metre, and is equal to 100000 g ergs.

Thus at Oxford a foot-pound is 13.565 megalergs, and a kilogrammetre 98.115 megalergs: at Manchester a foot-pound is 13.567 megalergs.

4. Energy. This is the power of doing work which a body or system of bodies possesses by reason of its state: it is of two kinds, kinetic and potential—the former due to the motions

of its various parts, the latter to the mutual actions between them.

Suppose that the small mass μ of the system at time t is at x, y, z , moving with the velocity v ; the axial-components of the effective forces are $\mu\ddot{x}, \mu\ddot{y}, \mu\ddot{z}$, and, if the components of the whole impressed force acting on it are X, Y, Z , the principle of virtual velocities gives

$$\Sigma \{ (X - \mu\ddot{x}) \delta x + (Y - \mu\ddot{y}) \delta y + (Z - \mu\ddot{z}) \delta z \} = 0,$$

whence on writing dx, dy, dz for $\delta x, \delta y, \delta z$ we have

$$\Sigma \mu (\ddot{x} dx + \ddot{y} dy + \ddot{z} dz) = \Sigma (X dx + Y dy + Z dz),$$

$$\text{or} \quad d\Sigma \cdot \frac{1}{2} \mu v^2 = \Sigma (X dx + Y dy + Z dz). \quad (1)$$

Now $\Sigma (X dx + Y dy + Z dz)$ represents the work done by the forces upon the system, or $-\Sigma (X dx + Y dy + Z dz)$ is the work done by the system against the forces to which it is subject, and, for the equation to be integrable, these expressions must be exact differentials; hence, if

$$-\Sigma (X dx + Y dy + Z dz) = d\chi, \quad (2)$$

we have as first integral

$$\Sigma \cdot \frac{1}{2} \mu v^2 - \Sigma \cdot \frac{1}{2} \mu u^2 = \Sigma \cdot f (X dx + Y dy + Z dz) = \chi_0 - \chi, \quad (3)$$

u being the initial velocity of the mass μ .

(i) Now suppose that the different parts of the system are rigidly connected together: then no work is done by the mutual actions of the parts, and the integral represents the work done upon the system by external forces only; equation (3), indeed, holds good, by D'Alembert's principle, even if the internal reactions are not included in X, Y, Z . Hence if the whole system is brought to rest by doing work against resisting forces—in which case X, Y, Z are negative—the value of v for each part becomes zero, and the total work done, viz.

$$-\Sigma \cdot f (X dx + Y dy + Z dz),$$

is equal to $\Sigma \cdot \frac{1}{2} \mu u^2$. The latter term, which depends only on the initial velocities of the different parts of the system, thus represents the total work that can be done by the system before it is brought to rest, *i.e.* the work it can do in virtue of its motion: it is therefore appropriately termed the *kinetic energy* of the system in its initial state. Hence the general equation

shews that for a rigid system (1) the work done against resistance is equal to its loss of kinetic energy, (2) the work done in altering the motion of its parts is equal to the increase of kinetic energy.

The most complicated motion of a rigid system can be reduced to a translation of its mass-centre and a rotation of the system about an axis through this centre, and, the mass of the whole being m , the velocity of translation \bar{u} , the radius of gyration about the instantaneous axis k , and the angular velocity ω , we easily find that

$$\Sigma \frac{1}{2} \mu u^2 = \frac{1}{2} m \bar{u}^2 + \frac{1}{2} m k^2 \omega^2 :$$

$\frac{1}{2} m \bar{u}^2$ is at any moment the kinetic energy of translation, and $\frac{1}{2} m k^2 \omega^2$ the kinetic energy of rotation. If at any moment there is no rotation, the velocity of all the parts is the same and equal to u , and the total kinetic energy $\frac{1}{2} m u^2$; or the kinetic energy of a mass m moving with velocity v is $\frac{1}{2} m v^2$.

As energy is measured by the amount of work it represents, the unit of energy is also the erg on the absolute system: hence also the kinetic energy in the last case, expressed in gravitation measure, is $\frac{m v^2}{2g}$.

(ii) Suppose now that the system is not rigid and is subject only to the mutual actions of its parts, there being no external forces: then the action between two particles μ, μ' , whose distance apart is r , being $\mu\mu'\phi(r)$, and all such forces being replaceable by their several axial components, the principle of virtual velocities gives

$$\Sigma (X dx + Y dy + Z dz) = \Sigma \mu\mu'\phi(r) dr = dU,$$

say. Hence, writing K for $\Sigma \frac{1}{2} \mu v^2$ and denoting the initial values by suffixes, we have by equation (3),

$$K - K_0 = U - U_0.$$

If U is the maximum value of U , and we take $P = U - U_0$, then P represents the maximum amount of work that the system is capable of doing on starting from the state corresponding to U_0 , or the work that the system *can* do by reason of its configuration—that is, by reason of the mutual actions which depend

on the positions of its parts: P is therefore called the *potential energy* of the system in that state.

(iii) In the above case we have further by substitution

$$K - K_0 = (U - P) - (U - P_0),$$

$$\text{or} \quad K + P = K_0 + P_0;$$

thus in a system of bodies subject only to the mutual actions of its parts the sum of the kinetic and potential energies—that is, its *total energy*—is a constant quantity. This theorem is called the *Principle of the Conservation of Energy*.

(iv) In the general case the impressed forces will consist of both internal and external actions, and, if the axial-components of the external impressed forces acting on the part μ are X' , Y' , Z' , the equation (1) becomes

$$\begin{aligned} dK &= dU + \Sigma (X'dx + Y'dy + Z'dz) \\ &= -dP + dW', \end{aligned}$$

say, where W' represents the work done by the external forces: hence if E is the total energy of the system

$$dW' = dK + dP = dE,$$

or for any system (1) the work done against external force is equal to its total loss of energy, (2) the work done in altering its state is equal to its gain of energy.

We have also from (3)

$$K - K_0 = \chi_0 - \chi,$$

or

$$K + \chi = K_0 + \chi_0,$$

the suffixes denoting the initial values. χ is called the *ergal* of all the forces, and thus the sum of the kinetic energy of a system and the ergal of the forces to which it is subject is a constant quantity.

If dW is the work done by the body against external forces we have obviously

$$d\chi = dP + dW. \quad (4)$$

(v) It is an interesting problem in connection with thermodynamics to determine the total kinetic energy of a body which moves as a whole and has also at the same time very rapid oscillations with respect to its parts. At time t let x, y, z be the coordinates of the mean position of an oscillating particle μ

whose real position is $x + \xi$, $y + \eta$, $z + \zeta$: then its velocity at this moment is given by

$$\begin{aligned} v^2 &= (\dot{x} + \dot{\xi})^2 + (\dot{y} + \dot{\eta})^2 + (\dot{z} + \dot{\zeta})^2 \\ &= (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + (\dot{\xi}^2 + \dot{\eta}^2 + \dot{\zeta}^2) + 2(\dot{x}\dot{\xi} + \dot{y}\dot{\eta} + \dot{z}\dot{\zeta}) \\ &= u^2 + v^2 + 2(\dot{x}\dot{\xi} + \dot{y}\dot{\eta} + \dot{z}\dot{\zeta}), \end{aligned}$$

if u is the velocity at this moment of the mean position of the particle, and v the velocity of oscillation. Hence the mean value of its kinetic energy during T , the periodic time of oscillation, is

$$\frac{\int_0^T \frac{1}{2} \mu v^2 dt}{\int_0^T dt} = \frac{\mu}{2T} \int_0^T v^2 dt = \frac{1}{2} \mu u^2 + \frac{\mu}{2T} \int_0^T v^2 dt,$$

since during this extremely short interval x , \dot{x} , y , \dot{y} , z , \dot{z} , u may all be considered constant, and

$$\int_0^T \dot{x}\dot{\xi} dt = \dot{x} \int_0^T d\xi = 0, \dots,$$

as the particle returns to its initial position. The total kinetic energy of the body may therefore be taken as

$$\Sigma \cdot \frac{1}{2} \mu u^2 + \Sigma \cdot \frac{\mu}{2T} \int_0^T v^2 dt,$$

that is, as the sum of the kinetic energy of its motion in space and the mean kinetic energy of the oscillations of its parts. We shall shew in Chapter III that the heat of a body consists in the oscillations of its ultimate atoms, whence it appears that the total kinetic energy of a hot body is that of its motion in space and that of its heat-oscillations together.

If the oscillations follow the pendulum-law so that

$$\xi = a \cos 2\pi \left(\frac{t}{T} + a \right), \dots,$$

$$\begin{aligned} \text{then } \int_0^T v^2 dt &= \frac{2\pi^2}{T^2} \int_0^T \{a^2 + \dots - a^2 \cos 4\pi \left(\frac{t}{T} + a \right) - \dots\} dt \\ &= \frac{2\pi^2}{T} (a^2 + b^2 + c^2), \end{aligned}$$

or the mean kinetic energy of oscillation—that which exhibits itself as heat—is $\pi^2 \Sigma \cdot \mu \frac{a^2 + b^2 + c^2}{T^2}$.

5. Stress. The stress on any part of a body in equilibrium is the force exerted upon it all round by the matter in contact with it, whether part of the same body or not, and is measured by the number of units of force that act upon unit area; that is, in absolute measure by the number of dynes per square centimetre, and in gravitation measure by the number of grams' weight per square centimetre. We shall notice only two kinds of stress that we shall meet with hereafter: they are both measured in the same way.

Longitudinal Stress or Tension acts in one direction only, producing compression or extension.

Hydrostatic Stress or Pressure is the same in all directions and acts normally to the surface of bodies: it is equivalent to three equal longitudinal stresses acting at right angles to each other. It is this stress to which we shall generally consider a body subjected, unless otherwise specified.

The units of pressure employed by engineers are gravitation measures: in Britain they are the weight of a pound per square foot or per square inch, which are equal to 479.05 and 68983 dynes per square centimetre respectively at Oxford; in metrical measure the unit is the weight of one kilogram per square metre, which at Oxford is equivalent to 98.115 in absolute units.

An unit much used in scientific tables is an *atmosphere*, defined as the pressure due to a barometric height of 76 c. of mercury at 0°c. in latitude 45° at sea-level; here g being 980.564 and the density of mercury 13.596 at 0°c., this pressure is equivalent to the weight of 1033.3 grams per square centimetre or to 1013226 in absolute measure.

A more scientific unit, and one which we shall always hereafter use under the name of an atmosphere, is the pressure of one megadyne per square centimetre. It is equivalent to a barometric height in latitude 45° of 75.008 c., or at Oxford of 74.963 c.

We must once more call attention to the inaccuracy of common talk. The measurement of pressures in *pounds per square inch*, &c. is quite improper, the accurate phrase being *pounds' weight per square inch*.

6. Strain. This is a general term to denote any alteration in the form or dimensions of a body. We shall consider two cases only, which correspond to the above varieties of stress.

Longitudinal Strain occurs when there is deformation in one direction only: it is measured by the ratio of the extension or compression of any line in the body in the direction of the strain to its original length.

Isotropic Strain occurs when the body after alteration is similar to its original form, that is, when it has undergone no deformation: it is the result of three equal longitudinal strains at right angles to each other, and is measured by the ratio of the change of volume to the original volume.

A strain, being the ratio of two similar magnitudes, is a numerical quantity.

7. Elasticity. The elasticity of a body is the resistance it offers to alteration in figure or dimensions, and is measured by the stress required to produce a strain: it is therefore the quotient of an increment of stress by the resulting strain when both are indefinitely diminished, and, being a magnitude of the same kind as stress, is measured in dynes per square centimetre. We shall notice the varieties only which correspond to the stresses and strains described above.

If a change of tension dT cause change of length dl in a length l , or a strain $\frac{dl}{l}$, the Longitudinal Elasticity is $l \frac{dT}{dl}$. This is also called *Young's Modulus of Elasticity*.

If change of hydrostatic stress dp cause change of volume $-dv$ in a volume v , or a strain $-\frac{dv}{v}$, the Volume-Elasticity is $-v \frac{dp}{dv}$.

8. Mechanical work done by or upon a body during a strain. This is measured per unit volume by the product of the strain into the average value of the component of the stress in its direction. We shall consider only two particular cases.

If a longitudinal stress T is the same at every point of a section ω perpendicular to its direction and causes deformation dl , the total work done is $\int T \omega dl$. In the case of a rod or

a cord stretched by the weight of m grams, $T\omega = mg$, and the work done is $mg\lambda$ ergs, where λ is the total change in length.

If a body of volume v is subject to a hydrostatic pressure p , which is the same at every point of the surface, the pressure on a small area dA is $p dA$: if the body increases in volume so that this pressure is overcome normally through a distance dn , the element of work done is $p dA dn$, and thus the element of work done by the whole surface is $p \oint dA dn$ or $p dv$; hence the whole external work is the integral $\int p dv$ taken between the proper limits.

The work is motor or resisting according as l and v increase or decrease, that is, as dl and dv are positive or negative.

Mr. Watt introduced a graphic mode of representing these integrals, both of which are of the same form since T and p are stresses, ωdl and dv changes of volume. If p is measured along the axis of ordinates and v along that of abscissæ, then

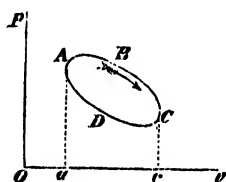


Fig. 1.

the connection between the successive states of a body may be represented by a curve, and $p dv$ will represent the infinitesimal area between the curve, the axis of volumes, and two infinitesimally distant ordinates. Hence if ABC represents the states through which a body passes from that denoted

by A to that denoted by C , the total work done by the body is represented by the area $ABCcaA$. Again, if CDA represents the successive states passed through by the body from that denoted by C to that denoted by A , work represented by the area $CDAacC$ is done upon the body, for it has been compressed. Hence if a body passes through the whole series of states represented by the closed curve $ABCD A$, the useful work done is the excess of the area $ABCcaA$ over the area $CDAacC$ (A and C being the points where the curve is touched by the extreme ordinates) or the area $ABCD A$: this work is done by the body if the expansion occurs under greater pressures than the contraction, as when the series follows the direction of the arrow,

that is, the direction of the hands of a watch; if the contraction occurs under greater pressures than the expansion so that the curve is traversed in the direction opposite to the arrow, the work is done *upon* the body.

These graphic representations of work are called *Indicator diagrams*, after an instrument called the Indicator which was invented by Mr. Watt to determine practically the work done by a steam-engine. M. Carnot gave the name *cycle* to such a series of modifications as is represented by a closed curve.

When a curve denotes the successive changes of state of a body, we shall say that the body *moves*, or that the modifications occur, *along* that curve.

On the subjects of this chapter the student is recommended to consult Professor Maxwell's *Theory of Heat*, chaps. iv, v, xxi: he will find therein also (p. 105) a full description of an improved indicator.

9. Virial. A dynamical idea of great importance has recently been introduced by Professor Clausius¹. If the small mass μ at (x, y, z) is acted upon by force F , whose axial components are X, Y, Z , we have

$$\mu \ddot{x} = X, \quad \mu \ddot{y} = Y, \quad \mu \ddot{z} = Z;$$

whence, since

$$\frac{d^2}{dt^2}(x^2) = 2\dot{x}^2 + 2x\ddot{x},$$

$$\text{we have} \quad \frac{1}{2}\mu \dot{x}^2 = -\frac{1}{2}Xx + \frac{1}{4}\frac{d^2}{dt^2} \cdot \mu x^2. \quad (5)$$

The mean value of each of these terms during any period t is found by multiplying it by dt , integrating for the time from 0 to t , and then dividing by t : thus, indicating mean values by bars, we have

$$\frac{1}{2}\mu \overline{\dot{x}^2} = -\frac{1}{2}\overline{Xx} + \frac{1}{4t} \left[\frac{d}{dt} \cdot \mu x^2 \right]_0^t. \quad (6)$$

Suppose now that the motion of the parts of the system is strictly periodic, and t is any multiple of their period; then the last term of (6) is zero, as at the end of a period each part returns to its original position. If the motion is not strictly

¹ *Pogg. Ann.* cxli. (1870) 124, trans. *Phil. Mag.* [4] xl. (1870) 122.

periodic, but of the kind termed *stationary*—i.e. when the parts do not continually move further and further from their original positions and their velocities do not continuously increase or decrease, the parts thus moving within a limited space and their velocities only fluctuating within certain limits—then the coefficient in square brackets (the difference between the values of $\frac{d}{dt} \cdot \mu x^2$ at the beginning and end of the period t) does not necessarily become zero for any value of t ; it cannot however increase indefinitely with the time, but can only fluctuate between certain limits, so that, by taking t large enough, we may render the last term of (6) negligible. In both these cases we have therefore

$$\frac{1}{2} \mu \overline{\dot{x}^2} = -\frac{1}{2} \overline{Xx}. \quad (7)$$

This mean value of the expression $-\frac{1}{2} Xx$ is called the *x*-component of the *virial of the particle*, and the equation shews that *for any particle of a system in stationary motion the mean kinetic energy relative to any direction is equal to the virial relative to the same direction*.

As similar equations in y and z hold, we have, if \bar{v} is the mean velocity of the particle,

$$\begin{aligned} \frac{1}{2} \mu \bar{v}^2 &= -\frac{1}{2} (\overline{Xx} + \overline{Yy} + \overline{Zz}) \\ &= -\frac{1}{2} F \rho \cos \epsilon = -\frac{1}{2} \overline{P\rho}, \end{aligned} \quad (8)$$

if ρ is the radius-vector of the particle, P the resolved part along it of the total force, and ϵ the angle between its direction and that of the total force F . Summing now over the whole system and writing \bar{K} for its mean kinetic energy, we have

$$\begin{aligned} \bar{K} &= -\frac{1}{2} \Sigma. (\overline{Xx} + \overline{Yy} + \overline{Zz}) \\ &= -\Sigma. \frac{1}{2} \overline{P\rho} : \end{aligned} \quad (9)$$

these right-hand expressions are called the *virial of the system*, so that the mean kinetic energy of a system in stationary motion is equal to its virial.

The general equation corresponding to (5) is obviously

$$\begin{aligned} \bar{K} &= -\frac{1}{2} \Sigma. (\overline{Xx} + \overline{Yy} + \overline{Zz}) + \frac{1}{4} \frac{d^2}{dt^2} \Sigma. \mu \rho^2 \\ &= -\Sigma. \frac{1}{2} \overline{P\rho} + \frac{1}{4} \frac{d^2}{dt^2} \Sigma. \mu \rho^2, \end{aligned} \quad (10)$$

so that the above theorem holds good whenever $\frac{d}{dt} \Sigma \cdot \mu \rho^3$ is independent of t : this is the case, for instance, when the system is rigid and moves with one point fixed, and again, when it consists of homogeneous incompressible fluid which always occupies the same portion of space though its molecules are in motion, since as each molecule leaves a spot it is replaced by another of equal mass.

In the general case there are both internal and external forces acting upon a system, and hence therefore an internal and an external virial. If R is the attraction between two particles μ, μ' at the points $(x, y, z), (x', y', z')$ respectively which are r apart, then for the internal forces

$$Xx + X'x' = \frac{x' - x}{r} R x + \frac{x - x'}{r} R x' = - \frac{(x' - x)^2}{r} R,$$

with similar equations in y and z : therefore

$$-\frac{1}{2} \Sigma \cdot (Xx + Yy + Zz) = \Sigma \cdot \frac{1}{2} Rr, \quad (11)$$

so that the internal virial is $\Sigma \cdot \frac{1}{2} Rr$; indeed, with a body in which innumerable atoms move irregularly but in essentially like circumstances, so that all possible phases of motion occur simultaneously, the difference between this mean value and the value of $\Sigma \cdot \frac{1}{2} Rr$ corresponding to any configuration of the system is inappreciable, so that the latter may be taken for the internal virial. The external virial is easily found in the case wherein the external forces consist of an uniform hydrostatic pressure p ; for then

$$\Sigma \cdot Xx = -p \iint x \cos a \, da = -p \iint x \, dy \, dz = -p \mathfrak{b},$$

where da is an element of area at the point (x, y, z) , a the inclination of the normal at this point to the x -axis, \mathfrak{b} the volume of the system; hence

$$-\frac{1}{2} \Sigma \cdot (Xx + Yy + Zz) = \frac{3}{2} p \mathfrak{b}, \quad (12)$$

and the external virial is $\frac{3}{2} p \mathfrak{b}$, both these quantities being constant. In this case therefore

$$\bar{K} = \frac{3}{2} p \mathfrak{b} + \Sigma \cdot \frac{1}{2} Rr, \quad (13)$$

or, as we may write it,

$$p \mathfrak{b} = \frac{2}{3} \bar{K} - \frac{1}{3} \Sigma \cdot Rr. \quad (14)$$

CHAPTER II.

Introductory Thermal Principles.

10. Measure of Heat. Whatever heat is, it is a measurable quantity; for its effect is generally proportional to the amount spent: thus twice as much heat is required to melt two grams of ice as to melt one, and two grams of coal give on combustion twice as much heat as one.

The usual thermal unit is defined as the amount of heat required to raise unit mass of water from the temperature of melting ice through one degree c. of temperature measured on the air-thermometer, and it is called a *calorie*. In this definition it is necessary to mention the initial temperature, as M. Regnault's experiments shew that

$$\theta + 0.00002 \theta^2 + 0.0000003 \theta^3,$$

or, according to later calculations by M. Bosscha¹,

$$\theta + 0.00011 \theta^2,$$

is the heat required to raise one gram of water from the temperature of melting ice through θ degrees c., and hence that

$$1 + 0.00022 \theta$$

is the amount required to raise the same mass at θ° c. through one degree. The real calculation gives 1.00011 instead of 1 for the term independent of θ ; this is merely because the first formula is empirical and thus not quite accurate: the difference is negligible.

11. Temperature. As temperature is a most important quantity in the dynamical theory of heat, it may be well to review the principles and conventions of the ordinary scales which depend on the properties of particular substances.

¹ *Pogg. Ann.* Jubelband (1874), 549.

When two bodies are together and one gains while the other loses heat, we say that they are at different temperatures: if neither gains or loses, we say that they are at equal temperatures. For the measurement of temperature we avail ourselves of the fact that bodies vary in volume or pressure as they gain or lose heat; we may thus take this change of volume or pressure, reckoned with a standard substance from a standard condition, or any function of it to define our scale of temperatures, and hence get an infinite number of systems. The following are the necessary or usual conventions:—

(1) Definition of rising temperatures: a body that loses heat to another by radiation or conduction is said to have the higher temperature. This convention is opposite to that of M. Delisle and of M. Celsius' original thermometer.

(2) Standard substance: alcohol for low, mercury for mean, air for all temperatures.

(3) Standard temperatures: those of melting ice and boiling water under standard pressure, as suggested by Newton.

(4) Standard pressure: for France 76 c. of mercury at the temperature of melting ice at sea-level in Paris, or 1013573 dynes per square centimetre; for England 29.905 in. of mercury at the same temperature at sea-level in London, or 1013252 dynes per square c.: the ratio of these pressures is 1.00032. A more scientific pressure would be one megadyne.

(5) Number of degrees between the standard temperatures: on Réaumur's scale 80, on Fahrenheit's 180, on Celsius' or the Centigrade scale 100.

(6) The variable used to define successive states of the thermometer: with alcohol and mercury this is the volume, with air it is either the elastic force under constant volume or the volume under constant pressure.

(7) Definition of a degree: Galileo's is used with the ordinary thermometer and with the air-thermometer when the volume under constant pressure is the variable employed; it is the following:—if the thermometric substance assumes volumes v, v_0 at the higher and lower standard temperatures respectively and n is the number of degrees between these temperatures,

one degree is defined by a change of volume equal to $\frac{v-v_0}{n}$, and thus the temperature T when the volume is V is given by

$$T = \frac{V-v_0}{v-v_0} n.$$

Dalton proposed to define a degree as corresponding to a change of volume $v_0 \sqrt[n]{\frac{v}{v_0}}$: in this case the temperature T corresponding to volume V is given by

$$\frac{V}{v_0} = \left(\frac{v}{v_0}\right)^{\frac{T}{n}} \quad \text{or} \quad T = \frac{\log V - \log v_0}{\log v - \log v_0} n.$$

In neither of these cases is the heat-value of a degree the same in different parts of the scale; it is more nearly so however in Galileo's than in Dalton's system, and hence the preference given to the former.

In the air-thermometer, when the elastic force under constant volume is the variable, if p, p_0 are the elastic forces at the standard temperatures, a degree is defined by the change of pressure $\frac{p-p_0}{n}$: hence for an elastic force P the temperature is given by

$$T = \frac{P-p_0}{p-p_0} n.$$

In this case the heat-value of a degree is very nearly the same in all parts of the scale, as shewn by M. Regnault's experiments on specific heat.

(8) The zero-point of the scale: Celsius and Réaumur take for this the lower standard temperature; Fahrenheit took the lowest temperature known in his time, that produced by salt mixed with snow.

(9) Absolute temperature on the air-thermometer: we might represent zero temperature by the state of a gas entirely deprived of heat, in which case its pressure is zero; if then ω denotes the change of elastic force measuring one degree, absolute temperature corresponding to pressure P is given by

$$\tau = \frac{P}{\omega}.$$

Taking these degrees the same as above, so that $\varpi = \frac{p-p_0}{n}$,
we have, if absolute zero is m degrees below ordinary zero,

$$m = \tau - T = \frac{P}{\varpi} - \frac{P-p_0}{\varpi} = \frac{p_0}{\varpi}.$$

The quantity $\frac{\varpi}{p_0}$, the reciprocal of m , is what is known as the coefficient of increase of elastic force at constant volume, and is generally denoted by α : its value is shewn by M. Regnault's exact experiments¹ to be neither the same for all gases nor constant for a given gas; it varies with the density,* and in the case of dry air may be represented by the formula²

$$\alpha = 0.00365343 + 0.00895 \rho,$$

where ρ is the density in grams per cubic centimetre. Thus the so-called *absolute* temperature depends on the substance used and is not constant. When the density is too small to affect the coefficient, we find $m = 273.72$, or absolute zero is in this case -273.72°C. : by a graphic construction from the experimental numbers Professor Rankine³ finds this value -274.6°C.

If we consider α constant, and measure temperature from the zero thus obtained, Boyle and Charles' laws combined may be written

$$\frac{pv}{\tau} = \text{const.},$$

a simple form first given by M. Clapeyron.

A perfectly absolute scale of temperature will be deduced in § 41 from thermodynamic principles: till then we must consider absolute temperature a function yet to be defined.

12. Characteristic equation of a body. The action of heat generally causes change in all the qualities of a body, elasticity, density, stress, temperature, refractive index, emissive power, conductivity, &c.: any two of these may however be taken in general as independent variables to characterize its state—*i.e.* the state of unit mass—and each of the others will

¹ *Mém. de l'Acad. des Sciences*, xxi. (1847) 110.

² *Phil. Trans.* cxliv. (1854) 357.

³ *Trans. R. S. E.* xx. (1853) 561.

be expressible as a definite function of the two selected ; thus between every three of the qualities there exists a relation

$$f(x, y, z) = 0,$$

and such relations are termed *characteristic equations*. These are only to be determined by experiment, and our knowledge is at present so incomplete that we are in a position to discuss that relation only which connects stress, density, and temperature ; and while herein, owing to the complexities of the general question, we introduce a simplification by considering the density, stress, and temperature the same throughout the body, and the stress a hydrostatic pressure, yet the problem of determining the exact form of the function still surpasses far the extent of our actual knowledge. One of the chief difficulties of the discussion arises from the experimental measurements that are the most easily and accurately made not being those most serviceable from a theoretical point of view.

We ought to explain what is meant by the 'stress of a body' : it is not the stress exerted on it by external bodies, but depends on the actual state of the body itself only, being the force it exerts at every point per unit area across any section in consequence of the motions or relative positions of its atoms ; and is only equal to external stresses in the case of equilibrium. This equilibrium we shall generally suppose to subsist.

It will be well here to introduce another quality, the *entropy* of a body, which is the property that remains constant when the body undergoes any change but without receiving or losing any heat : a more precise mathematical definition of entropy will be given in § 60.

We have thus to determine the form of the equation

$$f(p, v, t) = 0,$$

which is *par excellence* called the characteristic equation or the *equation of elasticity*, p being the stress (supposed a hydrostatic pressure) per unit area or the *specific pressure*, v the volume of unit mass or the *specific volume* (called also very expressively the *bulkiness* of the body by Professor Rankine and the *rarity* by Professor Maxwell), and t the absolute temperature. We may represent the equation graphically by means of a surface

if we take p, v, t as coordinates referred to three rectangular axes : then the determination of the relation between p and v for a given value of t amounts to finding the section of the surface by a plane perpendicular to the t -axis, and a determination of these sections for all values of t would give the complete surface, whence the sections by planes perpendicular to the other axes would be known. The three possible series of experiments here indicated are however so incomplete that it is necessary to make use of all, and not of one series only, to determine the surface. The surface differs for all bodies, with however three points of common likeness : (1) it exists only in the octant where p, v, t are all positive ; (2) it is terminated on the side nearest the origin on the axis of v , since the temperature and pressure diminish together indefinitely while the volume only approaches a finite minimum ; (3) on the other side it extends to infinity with a hyperbolic paraboloid as asymptotic surface, experiment shewing that, as the temperature rises, bodies approach more and more to the perfect state, defined below, wherein $pv = Rt$.

The equation assumes a different form in the *saturated* state of a body, or that in which all its parts are not in the same physical state : thus the solid and liquid forms may exist together simultaneously, the liquid and gaseous, or the solid and gaseous, but experiment shews that in these cases the pressure and the temperature cannot vary independently of each other, and the specific volume may vary while both p and t remain constant : the equation therefore breaks up into two, one

$$F(p, t) = 0,$$

and the other an expression for v in terms of either p or t and another variable. Let this variable be m , the proportion of the substance in the higher form in unit-mass of the mixture : then if s', s are the specific volumes of the body in the higher and lower forms respectively, we have

$$v = s'm + s(1-m) = s + (s' - s)m ; \quad (1)$$

and, the quantities s', s being functions of t which experiment must determine, this relation gives v in terms of t and m , or m in terms of v and t .

In contradistinction to the term *saturated* a body is called *superheated* when its temperature is higher than that corresponding to the state of saturation for the same pressure as given by the equation $F(p, t) = 0$. Thus slight compressions or expansions of superheated liquids and vapours will not alter the state of aggregation of the body, though they may tend to bring them nearer to the state of saturation.

Experiment has shewn that as the permanent gases are more and more rarefied they follow Boyle's law the more exactly, and their increments of pressure at constant volume are the more exactly proportional to their increments of temperature on the air-thermometer scale. We will define as a *perfect* gas a substance which exactly conforms to these laws, temperature being measured absolutely: its equation is easily found, as it is of the form $pv = \chi(t)$ and $\frac{\partial p}{\partial t} \equiv \frac{1}{v} \chi'(t)$ is to be independent of t or $\chi'(t)$ constant; representing then this constant by R we get

$$\frac{pv}{t} = R. \quad (2)$$

13. Choice of variables. It is not a matter of indifference which pair of the three variables p, v, t we take as independent in the equations we are about to form, though all three have been adopted.

(1) M. Clapeyron chose p and v , as the graphic representation in this case is the most convenient: there is an ambiguity however when the substance behaves like water.

(2) M. Saint-Robert takes p and t : this pair cannot however be used in the case of a saturated mixture, since p and t are not then independent.

(3) Professor Clausius and Sir W. Thomson use v and t , which pair, so far as we know, is applicable in all cases.

Hence it is best to use the last pair in general, though the others may always be employed when no ambiguity is thereby introduced (as in the discussion of gases): the first will however generally be used in diagrams.

14. Thermal capacities. The amount of heat which is required to change by unity any quality of unit-mass of a body

under given circumstances is called the *thermal capacity* corresponding to the given change; in three cases only have these capacities special names—the specific heat at constant volume, the specific heat at constant pressure, and the latent heat of expansion.

15. General equations of the effects produced by heat. For an increase dt of temperature when the volume remains constant, heat equal to $k dt$ is required, if k is the specific heat at constant volume; and similarly for an increase dv of volume when the temperature remains constant an amount of heat $l dv$ is required, if l represents the latent heat of dilatation. If the variations of t and v take place together, then the heat imparted dH is given by

$$dH = k dt + l dv. \quad (3)$$

It is obvious that l is the partial differential coefficient of H with regard to v when t remains constant; Professor Clausius therefore denotes it by $(\frac{dH}{dv})_t$, and M. Saint-Robert by $(H)_v$, similar symbols being used to express the other capacities. These are much more expressive than the single letter we employ, but present such a formidable appearance in the thermodynamic equations that the simpler symbols, even with the trouble of remembering their meaning, are preferable.

If a body undergoes an increase dt of temperature when the pressure remains constant, heat $K dt$ is absorbed, K —that is, $(\frac{dH}{dt})_p$, or $(H)_p$,—being the specific heat at constant pressure; and for an increase dp of pressure at constant temperature an amount of heat $L dp$ is required, L being a thermal capacity without specific name which is expressed by $(\frac{dH}{dp})_t$. If these variations occur simultaneously the total heat dH required is

$$dH = K dt + L dp. \quad (4)$$

If we represent the state of the body by the variables p and v , we get in a similar manner some such equation as

$$dH = p dp + v dv, \quad (5)$$

p , v being the partial differential coefficients of H with respect

to p when v is constant and with respect to v when p is constant respectively.

The student should find no difficulty in remembering the meaning of the above six symbols. With regard to other differential notation, we use the symbol d to signify *total* and the symbol ∂ to denote *partial* differentiation: thus $\frac{dp}{dt}$ means the total differential coefficient of p with respect to t , and $\frac{\partial p}{\partial t}$ its partial differential coefficient only: if no brackets are used in this latter case the variables are those we have adopted, v and t , that one being constant which does not occur in the expression; and if the variables are otherwise, that which is constant is denoted by a subscript outside a bracket;— $\frac{\partial E}{\partial t}$, $(\frac{\partial E}{\partial t})_p$, thus representing the partial differential coefficients of E with respect to t when v and p respectively remain constant. We shall further omit the bracket and subscript where p , v , t alone are concerned, the omitted variable being considered constant: thus in $\frac{\partial v}{\partial t}$, t and p are the variables considered, the latter being constant. In Chapter VIII the only variables used are m and t , and no brackets are employed.

16. Relations between the thermal capacities. By the characteristic equation we can express v as a function of p and t , and therefore

$$dv = \frac{\partial v}{\partial t} dt + \frac{\partial v}{\partial p} dp; \quad (a)$$

hence we have from (3) and (4)

$$\begin{aligned} K dt + L dp &= k dt + l dv \\ &= (k + l \frac{\partial v}{\partial t}) dt + l \frac{\partial v}{\partial p} dp, \end{aligned}$$

whence it follows that

$$K = k + l \frac{\partial v}{\partial t} \quad \text{or} \quad l \frac{\partial v}{\partial t} = K - k, \quad (6)$$

$$L = l \frac{\partial v}{\partial p}. \quad (7)$$

By similar methods we find

$$k = K + L \frac{\partial p}{\partial t} \quad \text{or} \quad -L \frac{\partial p}{\partial t} = K - k, \quad (8)$$

$$v = k \frac{\partial t}{\partial p} \quad \text{and} \quad v = K \frac{\partial t}{\partial v}. \quad (9)$$

Thus all the capacities are expressed in terms of the specific heats. We have made no supposition as to the units in which the heat dH and therefore all the different thermal capacities are measured; as however we shall shew in the next chapter that heat is equivalent to work, the megalerg therefore being a convenient unit, we shall consider the capacities all expressed in megalergs.

M. Regnault has experimentally determined in thermal units, and denoted by C , the specific heat under constant pressure for most substances: K represents the value of the same in work units, and, as shewn in the next chapter, is equal to $\mathcal{J}C$, where \mathcal{J} is 41.675. Denoting by c the specific heat of a body at constant volume in thermal units, we have also $k = \mathcal{J}c$.

The ratio of the specific heats, viz. $\frac{K}{k}$ or $\frac{C}{c}$, is a very important quantity: we shall denote it therefore by a single symbol κ . It is sometimes denoted by γ , which is not however so convenient or suggestive a letter.

From equation (a) we have, when v is constant or dv zero,

$$0 = \frac{\partial v}{\partial t} dt + \frac{\partial v}{\partial p} dp,$$

$$\text{or} \quad \frac{\partial p}{\partial t} = - \frac{\frac{\partial v}{\partial t}}{\frac{\partial v}{\partial p}}, \quad (b)$$

and similar relations; we have further

$$\frac{\partial v}{\partial t} = \frac{1}{\frac{\partial t}{\partial v}},$$

$$\begin{aligned} \text{and therefore by (b)} \quad & \left. \begin{aligned} \frac{\partial v}{\partial p} \cdot \frac{\partial p}{\partial t} \cdot \frac{\partial t}{\partial v} &= -1, \\ \text{and also} \quad \frac{\partial p}{\partial v} \cdot \frac{\partial v}{\partial t} \cdot \frac{\partial t}{\partial p} &= -1. \end{aligned} \right\} \quad (c) \end{aligned}$$

17. Volume-elasticities. The volume-elasticities of a substance with respect to two variations of condition, or rather their ratio, are important quantities: these are the elasticities when change of condition occurs without addition or loss of heat and when it occurs at constant temperature, *i.e.* the elasticities at constant entropy and at constant temperature (which Sir W. Thomson also terms the kinetic and static bulk-moduli of elasticity), and they are denoted respectively by ϵ_H (or ϵ_ϕ , see § 60) and ϵ_t .

We have by § 7,

$$\epsilon_t = \left[-v \frac{dp}{dv} \right]_t = -v \frac{\partial p}{\partial v}, \quad (10)$$

$$\epsilon_H = \left[-v \frac{dp}{dv} \right]_H = v \frac{\partial}{\partial v} = v \frac{\frac{\partial}{\partial v}}{\frac{\partial t}{\partial p}} = -v \frac{K}{k} \frac{\partial p}{\partial v}; \quad (11)$$

hence
$$\frac{\epsilon_H}{\epsilon_t} = \frac{K}{k} = \kappa, \quad (12)$$

or the ratio of the kinetic and static bulk-moduli is equal to the ratio of the specific heats under constant stress and constant strain.

The reciprocal of the volume-elasticity is called *the coefficient of compressibility*, and is generally denoted by β .

CHAPTER III.

Conservation of Energy.

FIRST LAW OF THERMODYNAMICS.

18. Heat a form of energy. It has been shewn that, if a system of bodies is subject only to the mutual actions of its parts, the total energy of the system remains constant, whatever changes occur within it. But in no machine does this condition seem to be exactly realized, even after allowance has been made for the energy spent in producing sound and the sensible vibrations of the machine : heat however is produced in all the cases when this apparent loss of energy occurs—as in the case of friction, percussion, &c., and this fact has led to the conclusion that heat is a form of energy. The chief arguments for this assumption and for the further hypothesis that heat is the energy of motion of the ultimate molecules of matter may be briefly stated as follows.

Heat is not material but a form of energy.

(a) A body has the same weight when hot as when cold, unless there has been oxidation : this may be shewn by weighing it in nitrogen or in a vacuum.

(β) Heat may be generated in any amount and cannot therefore be material : thus Count Rumford found himself able to boil any quantity of water by the heat produced in boring cannon.

(γ) The disappearance of mechanical energy is always accompanied by the production of heat.

(δ) The quantity of heat produced is exactly proportional to the quantity of work spent in producing it : this is shewn in § 24.

Heat is kinetic energy, at least partly.

(ϵ) When heat passes by conduction between bodies in contact at different temperatures, changes occur in their volumes, shewing that heat is accompanied by motion.

(ζ) If the bodies are separated interchange of heat is still observed; thus the energy of heat during its radiation between the bodies must exist in the kinetic form.

(η) The perfect identity of the laws of radiant heat with those of light as to reflexion, refraction, interference, absorption, polarization, double-refraction, &c. requires the same theory as to their nature.

Heat is molecular energy.

(θ) No motion of a body as a whole is observed as a consequence of heat: the motion must therefore be molecular and, at least in solid bodies, oscillatory.

The argument (η) may be expanded with advantage. If the radiation from a luminous slit be received on a screen after passing through a prism or grating, it is found in general to be decomposed into a multitude of rays of very varied refrangibility, some of which are visible and others invisible. Now each ray of the luminous spectrum produces not only the sensation of light in the eye, but also the sensation of heat when it falls on the nerves and chemical action in the haloid salts of silver and other substances: it is also found that any variation in its power of producing one of these effects entails a proportionate variation in its power of producing the others, whether the variation is caused by reflexion or refraction, interference or absorption, polarization or double-refraction, whence we conclude that all three effects are the result of one and the same action according as it works in one way or another; and as the phenomena of light can only be explained by the transversal vibrations of ether, we can only accept the same explanation for those of heat. This explanation must be extended further to the invisible radiation, as there is no difference whatever in kind between them: for by concentrating the invisible ultra-red rays by a lens on a solid body, or by passing

the invisible ultra-violet rays through quinine, we can transmute them into radiation visible to the eye—the phenomena of *calorescence* and *fluorescence*.

19. First Law of Thermodynamics. The really conclusive argument of those given above in proof of the dynamical nature of heat is (δ): this exact equivalence of heat and work is called the *First Law of Thermodynamics*. It was first stated by Sir H. Davy¹ in 1812, but dropped out of sight; Dr. Mayer² restated it in 1842 on theoretical grounds and determined the ratio between the units of heat and work—but by an assumption at that time unwarrantable; it owes its conclusive demonstration to Dr. Joule's experiments³ in 1843, which have been confirmed in their result by the widely differing methods of experiment he has since employed and which are given below. The ratio of the unit of heat to the unit of work—commonly called the *mechanical equivalent of heat*—is therefore generally denoted by J : its reciprocal or the ratio of the unit of work to the unit of heat—hence termed the *heat equivalent of work*—is often expressed by A . These ratios necessarily depend upon the units adopted.

DR. JOULE'S EXPERIMENTS.

20. I. By magneto-electricity. It is known that, if a soft-iron core wrapped with insulated wire forming a circuit be rotated between the poles of a magnet, induced currents are set up in the wire on the successive magnetization and demagnetization of the core. Dr. Joule, having already determined that if voltaic electricity pass along a resisting wire its energy is transformed into a heating-effect proportional to the resistance of the wire and to the square of the current intensity, shewed in 1843 that the induced currents conform to the same law, and further that the heating effect is in their case proportional also to the work spent in causing the rotation⁴. The

¹ *Elements of Chemical Philosophy*. London, 1812.

² *Lieb. Ann.* xlii. (1842) 233, trans. *Phil. Mag.* [4] xxiv. (1862) 371.

³ *Phil. Mag.* [3] xxiii. (1843) 263, 347, 435.

⁴ *Ibid.*

core he used consisted of soft-iron plates insulated from each other by oiled paper and bound together: this was wrapped with silk-covered copper wire and enclosed with water in a glass tube which was mounted horizontally between the poles of an electromagnet where it could be rotated by wheelwork about a vertical axis through its centre. The tube was covered

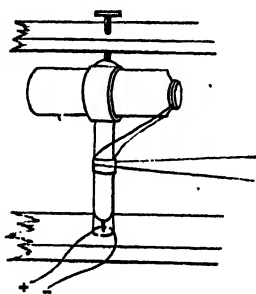


Fig. 2.

with tin-foil, slit horizontally to prevent external induced currents, and with flannel to prevent radiation and convection of heat. The terminals of the wire dipped into commutator grooves, containing mercury covered with water, which communicated with a galvanometer. In each experiment the tube was rotated for 15 minutes and the rise in temperature of the water measured. The necessary corrections were—

(1) For radiation, which was experimentally estimated at a quarter of the difference between the mean temperatures of the room and the water.

(2) For the heating of the water due to its agitation by the rotation and to possible conduction from the pivots: experiments made with the current of the electromagnet broken, when corrected for radiation, gave this correction.

(3) For the heat developed by the induced currents set up in the separate plates of the core: this was estimated by experimenting with the circuit of the wire round the core broken so as to prevent induced currents being generated in it, and by then applying the two former corrections.

The tube and core were made to revolve by the fall of weights, a correction being made for the weight required to move the whole with equal velocity without the inductive action. Work being expressed in gravitation measure, the mean of the experiments gave $\mathcal{J} = 45976$, or that one calorie of heat is equivalent to 45976 gram-centimetres of work.

21. II. By the friction of fluids. (a) By working¹ a piston perforated by a number of small holes in a glass cylinder containing water and measuring the work as in I, Dr. Joule in 1843 found $\gamma = 42464$.

(b) From 1845 to 1849 Dr. Joule experimented by another method² with the apparatus constantly improved. He finally used a cylindrical box of thin copper in which rotated a vertical spindle armed with eight brass paddles of complicated form, as shewn in the figure: four fixed vanes, so shaped as barely to allow passage to the paddles, prevented the fluid with which the box was filled being carried round by the motion, the energy of rotation being transformed by the consequent friction into heat: this effect could

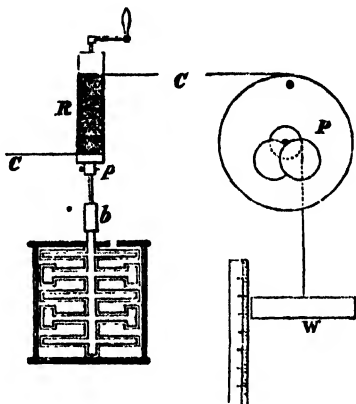


Fig. 3.

be read to $\frac{1}{3880}$ degree c. by a sensitive thermometer inserted through an opening in the lid. The paddles were set in motion by the fall of weights *W*, which, turning the axes of the pulleys *P* supported on friction-wheels, communicated a rapid motion to the roller *R* by means of the cord *C*: the roller could be detached from the spindle by removing the peg *p*, so that the weights could be wound up without moving the paddles—an operation performed 20 times in each experiment, which lasted about half-an-hour. The part *b* of the axis was of boxwood to prevent loss of heat from the box by conduction. The calculation is as follows:—

¹ *Phil. Mag.* [3] xxiii. (1843) 442, corrected in [3] xxvii. (1845) 206.

² *Phil. Mag.* [3] xxvii. (1845) 205, xxxi. (1847) 173, *C. R.* xxv. (1847) 309, *Phil. Trans.* cxl. (1850) i. 61.

Let θ be the observed rise in temperature of the fluid, τ the loss by radiation (estimated by experiment joined with Newton's Law of Cooling), m' the reduced water-capacity of the box and its contents; then the work done has raised the equivalent of m' grams of water through $\theta + \tau$ degrees, that is $m'(\theta + \tau)$ or \mathfrak{H} grams through 1 degree c.

Let H be the total fall of the weights, n the number of times the fall is made during an experiment, v the mean velocity of the fall; this velocity would be generated by a fall through $\frac{v^2}{2g}$, and hence the whole height through which the weights must have fallen to acquire the energy which is destroyed on the weights reaching the ground without a corresponding thermal effect in the box is $n \frac{v^2}{2g}$ or h say: thus $H - h$ is the effective fall. Let M be the mass of the moving weights, m the mass whose fall would turn the roller with equal velocity when the paddles are unattached (this measurement being attended with uncertainty): then the work done by the fall, expressed in gravitation measure, is $(H - h)(M - m)$. The elasticity of the string is found to do work E —called the *resilience*—after the weights have reached the floor, nE being thus done altogether, so that the total work gained by the fall of the weights is

$$(H - h)(M - m) + nE:$$

but part of this is spent in producing vibration in the apparatus—the energy of which V is difficult to estimate—and in producing sound, the energy of which S Dr. Joule measured by the work required to obtain from a violoncello a note of the same pitch and intensity: hence the total work spent in friction of the fluid is in gravitation measure

$$(H - h)(M - m) + nE - V - S \text{ or } \mathfrak{W} \text{ say,}$$

and the ratio of \mathfrak{W} to \mathfrak{H} gives \mathcal{F} .

The experiments performed were upon water, sperm-oil, mercury, and cast-iron working upon cast-iron in mercury, and in the last case only had S and V appreciable values. In one of the final experiments on water the following were the values

of the above quantities expressed in grams, centimetres, and degrees centigrade :—

$$\begin{array}{lll} \theta = 0.3196, & H = 3201.001, & M = 26318.223, \\ \tau = -0.0067, & v = 6.15, & m = 183.834, \\ m' = 6315.97, & n = 20, & E = 11701.287, \\ \mathfrak{M} = 1976.20; & h = 0.386; & \mathfrak{M} = 83880155; \end{array}$$

whence $\gamma = 42445$, or, when proper correction for vacuum is made, $\gamma = 42394$.

22. III. By the compression of gases. (a) When work is spent in compressing a gaseous fluid, evolution of heat occurs; and if no heat is absorbed or emitted by the gas during its variations in density, the work spent in producing a given thermal effect may be directly determined. The above condition is the principle unwarrantably assumed by Dr. Mayer; Dr. Joule however shewed in 1844 that it is appreciably satisfied by air, and he deduced 43781 as the mean value of γ given by his experiments¹.

Air was compressed by a force pump into a copper reservoir of 2237 c.c. capacity after having been drawn through a Ca Cl_2 drying tube and a leaden spiral tube immersed in water, which gave it a constant temperature. To collect the evolved heat the pump and reservoir were immersed in a known mass of water in a tinned-iron jar, which served as a calorimeter and was provided with double walls to diminish the loss of heat by radiation. After 300 strokes of the piston, when the pressure had become about 22 atmospheres, the rise in

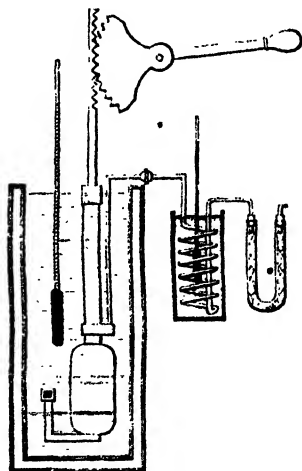


Fig. 4.

¹ *Phil. Mag.* [3] xxvi. (1845) 369.

temperature of the water was noted by a thermometer reading to $\frac{1}{100}$ degree c. The necessary corrections were—

(1) For radiation: this was estimated by experiment and Newton's Law of Cooling.

(2) For the heat due to the friction of the piston in the pump: this was estimated by working the piston 300 times without compressing air, and making an allowance for the difference in the mean pressures during the two experiments—a correction of much uncertainty.

As the pump was worked by the experimenter, the work could not be directly measured: but assuming Boyle's Law, $p v = p_0 v_0$, to hold in the case of air, we have by integration, as the temperature is nearly constant,

$$\text{Work} = \int p dv = p_0 v_0 \int_v^{v_0} \frac{dv}{v} = p_0 v_0 \log_e \frac{v_0}{v},$$

the suffixes denoting initial values. v_0 was determined by allowing the compressed air to expand till its pressure became p_0 : v is the capacity of the reservoir.

One of Dr. Joule's experiments gave $v_0 = 23482$ c.c., and $p_0 = 77.165$ c. of barometric pressure, or the weight of $77.165 \times 13.596 = 1049.13$ g. per sq. c. The gain of heat was equivalent to a rise of 1325.4 g. of water through 1 degree c., whence for gravitation measure

$$J = \frac{1}{1325.4} \times 1049.13 \times 23482 \times \log_e \frac{23482}{2237} = 43702.$$

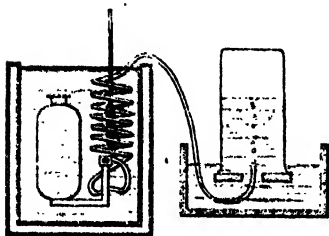


Fig. 5.

(b) When gases expand doing work, they experience a cooling and, the above condition being satisfied, the cooling effect is proportional to the work done. Dr. Joule determined the relation between these two effects in the following way¹:—

Compressed air was allowed to expand from the copper reservoir containing it

¹ *Phil. Mag.* [3] xxvi. (1845) 369.

through a long spiral tube into an inverted cylindrical glass vase standing over water: as it chased out the water it did work against the atmospheric pressure, and at the same time the water in which the reservoir and spiral were placed experienced a cooling. The gas was made to issue so slowly that the energy given to the water was negligible.

If p_0 is the atmospheric pressure and v_0 the volume of water displaced, the work done is equivalent to the raising of a column of the atmosphere 1 square centimetre in section through v_0 centimetres, and is therefore $p_0 v_0$ in gravitation measure. m being the water-equivalent of the calorimeter and all its contents and θ the cooling, $m\theta$ calories is the heat that has disappeared, and the ratio of $p_0 v_0$ to $m\theta$ is γ .

In one of the experiments $p_0 = 76.529$ c. of barometric pressure, or the weight of $76.529 \times 13.596 = 1040.5$ g. per square c.; $v_0 = 44621$, $m = 10682$, and $\theta = 0.0966$; whence $\gamma = 44992$.

23. IV. By the thermal effects of an electric current.

In 1867 the method adopted¹ was to pass an electric current through a resisting coil and measure the heat generated. The coil consisted of 366 c. of platinum-silver wire, bent double to prevent induction on its parts and then coiled in a spiral round a glass tube: it was provided with stout copper terminals and the whole was coated with shellac and mastic varnish. The calorimeter was of thin copper and, to diminish radiation as much as possible, was coated with tin-foil, then with two layers of silk net, and lastly with another layer of tin-foil: in it were inserted a thermometer and a stirrer driven by clock-work. Radiation and conduction by air were calculated from a series of interpolated experiments and allowed for.

If m is the reduced water-capacity of the calorimeter and all its contents and τ the corrected rise in temperature, $m\tau$ is the thermal effect during the time t . If H is the horizontal component of the earth's magnetic intensity and α the angle of deflection of the needle of a galvanometer placed in the circuit, $kH \tan \alpha$ will measure the intensity of the current, k being a

¹ *B. A. Rep.* (1867), i. 512.

constant that must be determined for each galvanometer by experiment. r being the resistance of the coil and t the time of the experiment, $(kH \tan a)^2 r t$ is (by Joule's Law) the work done in absolute measure, and the ratio of this quantity to $m\tau$ gives the corresponding value of \mathcal{J} .

The numbers in c. g. s. units for the best experiment were $k = 3.0426$, $H = 0.16957$, $\tan a = 0.59563$, $r = 989,530,000$, $t = 3600$, $m = 6081.96$, $\tau = 1.312$: whence \mathcal{J} is 4.216×10^7 , or, when corrected for vacuum, 4.212×10^7 . Dividing by 981.3, the value of g at Manchester, we find 42923 for the value of \mathcal{J} when work is expressed in gravitation measure.

24. Owing to the greater accuracy attainable in Series II of these experiments Dr. Joule concluded from it in 1849 that the integer 772 best represents the number of foot-pounds of work at Manchester that are required to raise a pound of water from 60° to 61°F. , and a recent set of experiments¹, also on the agitation of water, gives the number 772.55 for Greenwich, or 771.9 foot-pounds to raise a pound of water from 32° to 33°F. Multiplying then by $\frac{1}{2} \times 30.4797 = 54.8635$, we obtain 42349 as the number of gram-centimetres of work required to raise a gram of water from 0° to 1°C. , or 42349 is the value of \mathcal{J} when work is expressed in c. g. s. gravitation units. Further multiplication by 981.13, the value of g at Greenwich, gives 41,550,000 as the value of \mathcal{J} when work is measured in absolute units, or 41.55 if work is measured in megalergs. As the megalerg will be adopted in the following pages as the unit of work, we shall take 41.55 as the value of \mathcal{J} , or 1 calorie as equivalent to 41.55 megalergs.

25. M. Hirn's experiment. Of the many experiments made by M. Hirn² to evaluate \mathcal{J} we will describe one performed in 1859 which gives a result almost identical with the above. A cylindrical block of iron A and a prismatic block of stone B (faced on the end opposite A with a wrought iron plate) were suspended horizontally with their axes collinear, their ends being each supported by two strings so as to allow of their swinging only in a vertical plane through their axes: between the blocks when hanging in their lowest positions,

¹ *Phil. Trans.* clxviii. (1878).

² *Théorie mécanique de la Chaleur*, 3^{ème} éd. (1875), i. 95.

with its axis collinear with theirs, and just touched by them both, was placed with its mouth facing *A* a cylindrical piece of lead *C* partially bored out so as to form a cup. *A* was then raised through a known height and allowed to swing back and strike *C* just as reaching its lowest position it attained its maximum velocity: of the energy thus communicated to *C* part went in deforming it

—a quantity ultimately transformed into heat, part was transmitted to *B* making it swing back, *C* also joining in this motion, and part was given back to *A* causing its recoil. A fourth part must also have been

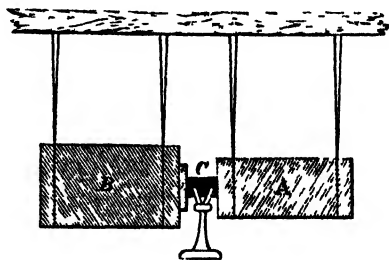


Fig. 6.

absorbed in deforming the faces of *A* and *B*, ultimately taking the form of heat; but this quantity is negligible from the hardness of wrought iron.

Let *m* be the mass of *A*, *m'* the mass of *B*, *μ* the mass of *C*, *h* the height through which *A* is raised and *h''* the height through which it recoils, *h'* the height through which *B* and *C* rise together: then the energy that is transformed into heat in *C* is $m(h - h'') - (m' + \mu)h'$ or $\frac{m(h - h'') - (m' + \mu)h'}{g}$ in gravitation measure.

The heating effect of this energy was determined by suspending *C* vertically, pouring into it a known mass of water at 0°c. immediately after the blow (at the same time starting a metronome), and then reading the temperature of this water every four minutes, noting also the temperature of the air. As the temperatures in question were low and their differences small, Newton's Law of Cooling was employed; whence, if *τ* is the excess in temperature of the water and lead over the air at time *x* after the blow, and *v* is the velocity of cooling,

$$\frac{d\tau}{dx} = -v\tau \quad \text{or} \quad \tau = \tau_0 e^{-vx},$$

the suffix denoting the initial value of *τ*, could the water and

lead have immediately attained equilibrium of temperature. The values of τ after times $x, 2x, 3x, \dots$ being $\tau_1, \tau_2, \tau_3, \dots$, we find

$$\frac{\tau_1}{\tau_0} = \frac{\tau_2}{\tau_1} = \frac{\tau_3}{\tau_2} = \dots,$$

and therefore
$$\tau_0 = \frac{\tau_1^2}{\tau_2} = \dots = \left(\frac{\tau_1^{n+1}}{\tau_{n+1}} \right)^{\frac{1}{n}};$$

or if, the temperature of the air being a , the temperatures of the lead corresponding to the excesses τ_0, τ_1, \dots are t_0, t_1, \dots , we have

$$t_0 = a + \frac{(t_1 - a)^2}{t_2 - a} = \dots = a + \frac{(t_1 - a)^{\frac{n+1}{n}}}{(t_{n+1} - a)^{\frac{1}{n}}}.$$

If θ is the initial temperature of the lead, and μ' the mass of the water, the energy given by the blow has raised the lead through $t_0 - \theta$ and the water through t_0 degrees, and is thus equal to $\mu C(t_0 - \theta) + \mu' t_0$ or \mathfrak{H} calories, C being the specific heat of lead: \mathfrak{Y} is thus the ratio of \mathfrak{H} to \mathfrak{W} .

In one of M. Hirn's experiments $m = 3.5 \times 10^3$, $m' = 9.41 \times 10^3$, $\mu = 2948$, $h = 116.6$, $h' = 10.3$, $h'' = 8.7$, whence $\mathfrak{W} = 28042336$; also $a = 8.8^\circ$, $t_1 = 12.1^\circ$, $t_2 = 11.75^\circ$, whence $t_0 = 12.49^\circ$; and again $\mu' = 18.5$, $\theta = 7.873^\circ$, $C = 0.03145$, and therefore $\mathfrak{H} = 659.351$: hence $\mathfrak{Y} = 42530$, work being expressed in gravitation measure.

CONSTITUTION OF BODIES.

26. Intrinsic energy. Heat thus being energy, the capacity of a system for doing work is altered as well by its loss or gain of heat as by the expenditure of mechanical work upon or by it. The total work that a body can do in virtue of its actual condition without any supply of energy in any form whatever from without is called its *intrinsic energy* and is denoted by E (often also by U); it appears also in Sir W. Thomson's papers as the *mechanical energy* and in Professor Kirchhoff's as the *work-function* of the body, while Dr. Zeuner calls it the *internal work*. It is obviously impossible to measure the intrinsic energy of a body, since for this purpose we must rob it of all its heat: we are really concerned however only with the variations of the intrinsic energy, and these are at once

measured by determining the amount of energy in all forms that enters and the amount that leaves the body during the given change.

As the energy of a system is presumably both kinetic and potential, the intrinsic energy of a body has been broken up into two corresponding parts, called the *sensible heat* and the *internal work*. These and their variations are however beyond the reach of experimental measurement, and their consideration belongs entirely to molecular science; still, as they help us to form a conception of thermal phenomena, we shall briefly review them and the theories of the constitution of bodies on which they are founded, at the same time remembering that all is pure assumption.

27. Constitution of bodies. Matter is generally supposed to be made up of indivisible unalterable particles called *atoms* which are, at ordinary temperatures at least, separated by distances very large in proportion to their size; but they are so small that an enormous number are contained in what would appear to us an infinitely small mass—in fact their estimated diameter is one hundred millionth of a centimetre. There are supposed to be as many different kinds of atoms as there are elementary chemical substances, and these all attract each other and may therefore form groups which are called *molecules*: thus, according to the different atoms grouped together is one or another chemical compound formed, and according to the mode of grouping of similar atoms is one or another allotropic form produced. The grouping together of two atoms of oxygen for instance is supposed to form the ordinary molecule of oxygen, while the anomalous grouping of the oxygen atoms in threes gives ozone; and again the differences between the four isomeric conditions of hydrogen tartrate $C_4H_6O_6$ —one that rotates the plane of polarization of light to the right and is therefore called hydrogen dextro-tartrate, another rotating it to the left and called hydrogen levro-tartrate, a third made up of the other two and called hydrogen racemate, which is inactive, and a fourth which is also inactive—are supposed to be due to differences in the grouping of the C, H and O

atoms. The atoms of a molecule so defined can obviously have both vibratory and rotatory motions.

The interatomic spaces have been supposed to contain ether atoms which are much smaller and which repel each other while they are attracted by matter: they will thus form atmospheres around the material atoms, the density of which decreases from the centre outwards. Professor Rankine uses the term *atom* to signify the central nucleus together with its atmosphere: M. Redtenbacher coins the special name *dynamid*. The movements of the particles of ether must obviously be confined within the boundary of the atmosphere.

Thus when radiation falls on a body, the atoms, their atmospheres, or both may be set in motion and the body is warmed: its atoms too, or their atmospheres, can put the external ether in motion and the body then radiates.

Professor Rankine in his hypothesis of molecular vortices considers that a body is solid when the atmospheres are so much condensed about the nuclei that their mutual repulsion is very small compared with the attraction between the nuclei: that it is liquid when the atmospheres are less condensed, so that the attractive action between the nuclei produces merely a cohesive force sufficient to balance the repulsion between the atmospheres; and that in a gas the action between the nuclei is almost insensible.

Professors Clausius and Maxwell, working out M. Bernoulli's idea, reject the notion of atmospheres, the ether atoms not differing except in mass from those of matter, and consider the difference of physical state to depend on the distances between the molecules: in the solid state they are so close together as not to be able to move far away from their mean positions, so that their motion is oscillatory; in the liquid state one molecule can move out of the sphere of attraction of another, but only to come into the sphere of attraction of a third, thus moving with an irregular progressive motion; in the gaseous state the molecules are so far apart as to exercise but slight actions on each other, and they therefore progress in straight lines until they collide against each other or

come into each other's sphere of attraction and take new directions.

28. Sensible heat. Professor Rankine considers, with Sir H. Davy, that the sensible heat S of a body is the kinetic energy of the atmospheres the particles of which are in oscillatory or progressive motion, and to connect this hypothesis with the undulatory theory of radiation he introduces the further supposition that radiation is effected by the motion under their mutual actions of the nuclei vibrating independently of their atmospheres.

On the other theory the sensible heat is the total kinetic energy of the system: this is a more complicated quantity, as the kinetic energy of a molecule is the sum of the kinetic energies (1) of the vibratory or rotatory movements of the atoms themselves, (2) of the rotatory movement of the molecule as a whole, (3) of its motion of translation, (4) of the motion of any molecules of ether that may be entangled in it. This is the preferable assumption.

29. Internal work. As the atoms in any molecule attract each other, and also one molecule attracts another, work must be spent to increase the mean distances either of the atoms or the molecules from each other: this work is however not lost, for the atoms or molecules by reason of their mutual actions are able to do just as much work in returning to their original configuration: the work is therefore stored up as potential energy of molecular separation. The work that is done against molecular forces only in increasing the mean distances of the atoms or molecules from each other and in overcoming molecular forces when the motions are increased is called the *internal work* and denoted by I .

If a body continuously receives heat, it finally assumes the perfectly gaseous state; and as changes of density in this state entail no internal work whatever the temperature (as shewn in § 63), it follows that the same amount of work \mathfrak{J} must be done against molecular actions to bring a given body from the state in which it is absolutely cold—in which its atoms and molecules are absolutely motionless and in such positions that

the attractions and repulsions balance each other—into a state in which it is perfectly gaseous, and this is the maximum amount of internal work that can be done in the body or is the maximum potential energy of molecular separation that it can possess.

30. External work. When a body expands against the action of external forces it does *external work* in overcoming them: if on the contrary it contracts and the external forces are such as tend to cause compression, then these forces do work upon it. We shall denote it by W , which is positive when the body does work.

GENERAL EQUATION OF EQUIVALENCE.

31. We can now construct an equation expressing the First Law of Thermodynamics, and it will be simpler if we measure quantities of heat dynamically, that is, in megalergs, rather than in calories, as by this means we avoid the introduction of either \mathcal{J} or A into our expressions: this is the method adopted by Professor Rankine. In this case we obviously cannot make direct use of the tables of different heat quantities, such as specific and latent heats, that have been constructed by M. Regnault and other experimenters; we must first multiply the numbers by 41.55 to reduce them from calories to megalergs.

We shall consider the modifications in the molecular motions only of a body: if change also is produced by heat in the motion of a body as a whole—its visible or *external* motion, as M. Zeuner terms it—we shall leave out of consideration that part of the heat which is concerned with such change, except in special cases.

Consider heat dH communicated to unit-mass of a body: there ensue in general—

- (1) An increase dE of the intrinsic energy of the body:
- (2) External work dW done against external forces:
- (3) A communication of kinetic energy dV to external bodies: •
- (4) An amount of heat dR communicated to external bodies by radiation, conduction, &c.:

Hence the conservation of energy gives

$$dH = dE + dW + dV + dR. \quad (1)$$

This is the most general equation, but we shall generally simplify it by supposing $dR = 0$, or that the body is never in presence of others whose temperature is not infinitely near its own, and $dV = 0$, or that all changes of volume occur with exceeding slowness: this latter condition requires also that the stress^o exerted by any part of the body should never differ more than infinitesimally from the external pressure acting upon the same part. We shall consider too that no part of the external work dW takes the form of electric or magnetic energy. We thus have

$$dH = dE + dW. \quad (2)$$

For solid bodies dE is by far the larger term on the right-hand side of the equation, dW being insignificant; dV is somewhat larger for liquids; but in gases it is dE that is nearly insensible. Of course any of the above quantities may be zero or negative; thus dH is negative if the body loses heat instead of gaining it, and it is 0 if there is neither gain nor loss; dW is negative if the body contracts—a phenomenon which generally occurs on the subtraction of heat, but also on the addition of heat in the case of water between 0° and 4°C ., of certain aqueous solutions, and of silver iodide between 10° and 70°C .

dE is a perfect differential, since the energy of a body depends only upon its actual state, and not upon the mode of its attaining that state; but dW depends on the relations between the stress and the expansion at the different points of the body, and thus not only on the initial and final states of the body but also on the whole series of states through which it has passed: hence dH is not a perfect differential, and for the integration of equation (2) a relation connecting the stress and expansibility at every point must be given. It is on this point that MM. Laplace and Poisson have gone wrong from their acceptance of the material theory of heat and their consequent assumption that dH is a perfect differential: the true case was first distinctly stated by M. Clausius. Given the necessary relation, we get by integration

$$H = E - E_0 + W. \quad (3)$$

According to Professor Clausius' hypothesis, dE is in general made up of—

(1) An increase of the molecular kinetic energy, or an increase of sensible heat dS :

(2) Internal work dI done against molecular forces, partly in augmenting the kinetic energy of the molecules and their atoms (whether this is done by an increase in their amplitudes of oscillation or a superposition of new forms of vibration) and partly in increasing their mean distances from each other:

whence the general equation becomes

$$dH = dS + dI + dW, \quad (4)$$

wherein dS and dI would both be perfect differentials. $dS = 0$ during fusion and vaporization under constant pressure, as the temperature then remains constant.

Following Professor Clausius¹ further we may simplify this equation by writing dD for $dI + dW$, and we get

$$dH = dS + dD. \quad (5)$$

dD is called the *work of disgregation*, and represents on this hypothesis the whole work done, both internal and external, during the given change of volume: it is obviously not a perfect differential. We shall consider this method later in § 59.

We shall in general suppose, unless express mention is made otherwise, that the stresses consist simply of a hydrostatic pressure which is the same at all points: if then p is this pressure per unit area and v the specific volume of the substance, $dIV = p dv$, and the relation between simultaneous values of p and v must be given. We have then

$$W = \int_{v_0}^v p dv. \quad (6)$$

32. Thermal lines. The loci of the points on the characteristic surface which represent the successive conditions of a body that alters its state under given circumstances are called *thermal lines*. We distinguish with special names (due to Professors Rankine and Gibbs) the following which are the most important.

¹ *Pogg. Ann.* cxvi. (1862) 73, trans. *Phil. Mag.* [4] xxiv. (1862) 81.

Adiabatic lines, or lines of no transmission, are the thermal lines denoting the states of a body that is altered without communication or abstraction of heat. As no vessel can be made perfectly impermeable by heat, these lines can only approximately be determined by experiment. In this case $H = 0$, and equation (3) gives

$$W = E_0 - E, \quad (7)$$

or the substance loses intrinsic energy equal to the external work done.

Isopiestic lines, or lines of equal pressure, are the curves that represent the states of a body when its pressure is constant: their orthogonal projections on the plane of p, v are therefore always parallel to the axis of v . In this case $p = p_0$, and equation (6) gives

$$W = p_0(v - v_0).$$

These lines are also called *isobars*.

Isometric lines, or lines of equal volume, denote the states of a body in which its volume is constant: their projections on the plane of p, v are similarly always parallel to the axis of p . In this case $dv = 0$, or

$$W = 0,$$

all the work done being therefore internal.

Isothermal lines, or lines of equal temperature, connect the different states of the body wherein its temperature is constant. As an increase of pressure must produce a diminution of volume, otherwise an unstable condition will be realized, isothermals are convex towards the origin of co-ordinates. On the above hypothesis we have in this case $dS = 0$, and equation (4) reduces to

$$dH = dI + dW.$$

If the substance is in the saturated state the isothermals coincide with the isopiestic.

Isenergetic lines, or lines of equal energy (called also by M. Cazin *isodynamic* lines), are given by the equation $dE = 0$; in this case therefore

$$W = H,$$

or all the heat put into the body is spent in external work. The zero isenergetic, or line of no energy, coincides with the zero isothermal; for, when $E = 0$, both S and I must be zero too, as neither can be negative.

Isentropic lines, or lines of equal entropy, denote the successive states of a body wherein the entropy remains constant. From the definition of this property in § 12 it follows that the isentropics coincide with the adiabatics.

The above names are generally given, not to the actual lines we have described, but to their orthogonal projections on the plane of pv ; for by these the work done during the corresponding transformations may be at once graphically represented as in § 8: hence we shall also for convenience denote the projections by the above terms, calling the actual curves on the characteristic surface the *real* thermal lines. If then a thermal line is defined by $F(p, v) = 0$, the corresponding real thermal line is the intersection of the cylinder $F(p, v) = 0$, whose generating lines are parallel to the axis of t , with the characteristic surface of the substance $f(p, v, t) = 0$.

No two real thermal lines of the same type can intersect each other, as they imply an essential difference in the states of the body characterised by them: hence, if we are given a model of the characteristic surface of a body with its real thermal lines traced thereon, we can always immediately determine its pressure, density, temperature, energy or entropy corresponding to a state defined by any two of them: for the intersection of the two curves characterising this state determines a point through which must pass all the curves corresponding to the other qualities. The same is generally true if we are given a complete diagram of the projections of these curves on the plane of pv —or, according to the above nomenclature, a complete diagram of the thermal lines: Professor Rücker has however shewn that in certain cases, which we shall examine at length in § 44, two isentropics may cut each other, and therefore also two thermal lines of any the same type.

The r -axis is asymptotic to all isothermals and adiabatics; for indefinite expansion brings every body approximately into the perfectly gaseous state, in which p is infinitely small for infinite values of v : it is asymptotic also to all isenergics, since these in the case of a perfect gas coincide with the isothermals, as shewn in § 63.

33. Adiabatics. Where an adiabatic A crosses an isothermal I , it is inclined at the greater angle to the axis of volumes: for if a substance that expands as its temperature rises is enclosed in a vessel and then slightly compressed, the work spent in the compression is transformed into heat, which is retained if the walls are perfectly impermeable by heat and, by tending to increase the volume of the substance, increases its resistance to compression and causes a greater increase

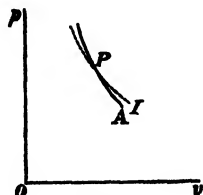


Fig. 7.

of pressure than if it were allowed to escape and the temperature to remain constant; and again, if the substance contracts as its temperature rises, compression lowers the temperature, and the heat that enters in consequence from without, if the walls are permeable by it, tends to produce a greater compression than if the walls were perfectly non-conducting. Professor Maxwell¹ shews that this is an illustration of the general principle that for any alteration in the state of a body subject to constraint greater force is required than for the same alteration when there is no constraint.

Professor Rankine² has applied the properties of adiabatics to the graphic representations of the energy of a body, the heat spent in any operation, &c.: we give the most important of these, which depend on the following theorem.

Suppose a body initially in the state A (Fig. 8) to expand without loss or gain of heat, that is, along the adiabatic Aa , doing work against external pressure that is at all times only infinitesimally less than its own. Now when the volume is infinitely large the work that is done by further expansion is infinitely small, as Ov is asymptotic to Aa ; hence the area bounded by the ordinate Aa , the adiabatic Aa , and the zero isopiestic Ov , has a finite value, and represents the maximum amount of work that can be done by the body, or, by equation (7), its maximum change of intrinsic energy, when it expands

¹ *Theory of Heat*, 4th ed. (1875), 131.

² *Phil. Trans.* cxliv. (1854) 115.

as above. But, the expansion being indefinite, the body finally assumes the perfectly gaseous state, in which changes of density

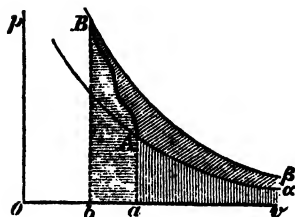


Fig. 8.

entail no internal work (as shewn in § 63); hence the external work is ultimately done entirely at the expense of the molecular kinetic energy, that is, the temperature of the body, which therefore finally becomes infinitely small, so that the intrinsic energy of the body, after infinite expansion adiabatically, is simply its

potential energy \mathfrak{I} (see § 29). Thus we arrive at the theorem that, if E_0 is the intrinsic energy of the body in the state A ,

$$\text{area } AavaA = E_0 - \mathfrak{I},$$

or the intrinsic energy of the body in the state A is represented by the sum of the area $AavaA$ and a constant area equal to \mathfrak{I} .

It is often assumed by a mistake that the intrinsic energy of the body in its infinitely extended state and cold is zero instead of \mathfrak{I} : this mistake does not however affect the following results as they depend on differences only of the values of E , or on differences of areas such as $AavaA$, so that \mathfrak{I} disappears. We shall always consider areas to be positive if traversed in the direction of motion of the hands of a watch.

(1) *The change of intrinsic energy of a body in passing from one state to another.*

At A the intrinsic energy is $AavaA + \mathfrak{I}$, and at B it is $B\beta vbB + \mathfrak{I}$: the change of intrinsic energy in passing from A to B is therefore the difference between these areas, or the area $AabB\beta aA$, which is independent of the path AB . Our results will not differ more than infinitesimally from the truth if we suppose that all adiabatics touch the zero isopiestic at the same point.

(2) *The heat required to transform a body by any path from one state to another.*

This is represented by the area included between the path-

curve and the adiabatics through the initial and final states : for in the path AB it is the sum of the increase of energy $AabB\beta aA$ and the work done $ABbaA$, and is thus the area $AB\beta aA$, regard being paid to the signs of the areas. In the diagram this area is positive, thus denoting heat absorbed (the body passing from a lower to a higher adiabatic), and it lies to the *right* of the direction of change AB ; if the direction of the change were from B to A , heat represented by the negative area $BAa\beta B$ which lies to the *left* of BA must be emitted: hence

(3) *To determine in any transformation whether heat is absorbed or emitted.*

Draw the adiabatic through the point representing the initial state : if the path-curve lies above the adiabatic, heat is absorbed; if under, emitted.

(4) *The heat supplied when the points representing the initial and final states are on the same adiabatic.*

This is the area between the path-curve and the adiabatic, as follows at once from (2) when the second adiabatic is made to coincide with the first: this area is positive if the body passes from the curve to the adiabatic in the direction of the hands of a watch.

The above method requires an infinite diagram : M. Cazin¹ has removed this objection by introducing isenergies—a slight complication which is however a convenience on the whole. Let the isenergetic through the initial state A cut the adiabatic through the final state B in the point C : then the area $ABbaA$ represents the work done during the passage of the body from A to B , the area $BCc\beta B$ represents the change in its intrinsic

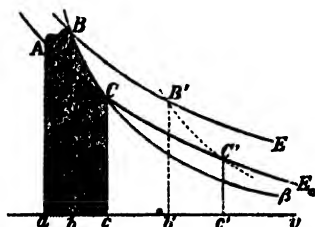


Fig. 9.

¹ *Théorie élémentaire des machines à air chaud.* (1865).

energy, and the area $ABCcA$ the heat that has been supplied along the path AB . For

$$E = BC\beta v b B + \mathfrak{J},$$

and $E_0 = C\beta v c C + \mathfrak{J}$, since C is on the isenergetic through A ; hence $E - E_0 = BCc b B$. We may further note that it is not necessary to draw the particular adiabetic that passes through B provided we can draw the isenergetic that passes through it; for if any other adiabetic $B'C'$ is drawn, the area $B'C'c'b'B'$ equally represents the intrinsic energy acquired by the body in passing from A to B , or, indeed, in passing from any point on the one isenergetic to any point on the other. The signs of these areas determine the real phenomena.

CHAPTER IV.

Transformation of Heat.

CARNOT'S PRINCIPLE.

34. Heat engines. A machine by which heat can be continuously transformed into work is called a *heat engine*. We have seen that when heat is given to a body an equivalent amount of work is done, partly internal and partly external, but work cannot be continuously performed without a reciprocating motion of some kind in the engine: air, for instance, enclosed in a cylinder by a piston and heated will expand and press out the piston, thereby doing work, but no more work can be done when the piston has reached the end of its stroke till by some means it has been brought back to its former position. For this action work must be spent by the engine if it is self-acting, so that useful work is not done in amount corresponding to the whole amount of heat communicated; part of this heat is therefore untransformed and must have been given up as heat to other bodies if the air is brought back to its original condition, or, as it is said, if a *complete cycle of operations* has been performed. The bodies from which the working substance of the engine (in the above case air) receives heat are called *sources*, and those to which it gives up heat are called *refrigerators*; these terms are often replaced by *furnace* and *condenser* in the case of vapour engines.

35. Carnot's cycle. The simplest cycle for an engine to perform is that devised in 1824 by M. Carnot¹, and though it cannot be practically realized, our reasonings are not thereby

¹ See Clapeyron's *Mémoire de la puissance motrice de la chaleur*, *Journ. de l'Ecole Poly.* xiv. (1834) 153, or Thomson's *An Account of Carnot's Theory*, *dec.*, *Trans. R. S. E.* xvi. (1849) 541. Carnot's original tract, *Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance*, is not procurable: it has however been reprinted in *Ann. de l'Ecole Norm.* [2] i. (1872) 293.

invalidated. Heat is supposed to be taken in by the working substance of the engine, always at one constant temperature and to be given out always at another constant temperature: thus there are one source and one refrigerator only whose temperatures are not to vary with the losses or gains of heat that they experience—a condition which is realized by a vapour in contact with its liquid at constant pressure, or when the source and refrigerator are very large; the engine moreover

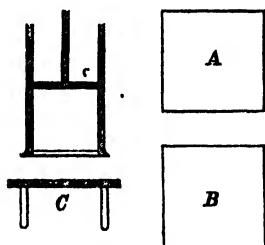


Fig. 10.

must be so constructed and of such materials as to prevent loss or gain of heat except, at these temperatures. M. Carnot's hypothetical engine consists of a cylinder the piston and sides of which are perfect non-conductors while the bottom is a perfect conductor, the whole possessing no capacity for heat: the source and refrigerator

are formed of two stands *A* and *B* respectively, and *C* is a third stand of perfectly non-conducting material which has no capacity for heat. If the cylinder stands upon *A* or *B*, the temperature of the substance will be constant however its state changes; and if it stands on *C*, no gain or loss of heat is possible.

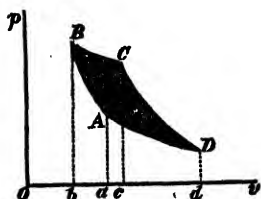


Fig. 11.

be at the temperature *t* of the refrigerator and be represented as to pressure and volume in its initial state by *A* in the diagram. The operations are as follows.

(1) Spend work in compressing it without loss of heat till its temperature rises to *T*, that of the source: during this process the cylinder rests on the non-conducting stand. If E_0 and E_1 are the intrinsic energy in the initial and final states and W_1 the work spent, equation (3), § 31, gives

$0 = E_1 - E_0 - W_1,$

and the successive states of the body are given by the adiabatic AB .

(2) Let it expand and do external work W_2 , receiving heat H from the source so that its temperature is always constant and equal to T : during this process the cylinder rests on the source-stand, and the successive states of the body are represented by the isothermal BC . If E_2 is the intrinsic energy in the final state C , we have

$$H = E_2 - E_1 + W_2.$$

(3) Let it expand further and do external work W_3 without receiving heat until its temperature falls again to t , that of the refrigerator: the adiabatic CD denotes the successive states of the body during this operation, in which the cylinder is again upon the non-conducting stand. If the intrinsic energy in the final state D is E_3 , then

$$0 = E_3 - E_2 + W_3.$$

(4) Expend work W_4 in compressing the substance at the constant temperature t until it returns to its original condition after giving up heat h to the refrigerator: in this case the cylinder is placed on the refrigerator-stand, and the successive states of the body are given by the isothermal DA . We have therefore

$$-h = E_0 - E_3 - W_4.$$

Adding together these four equations, we have

$$\begin{aligned} H - h &= -W_1 + W_2 + W_3 - W_4 \\ &= \text{area } ABCDA = W, \end{aligned}$$

the total external work done, no change of intrinsic energy on the whole having occurred, since the body has performed a complete cycle.

M. Carnot, assuming, though not without doubts, the material theory of heat, took $h = H$, since on the whole no heat is gained or lost by the body in the cycle, and considered the work done as due to the fall of heat from a higher to a lower temperature, just as work may be done by the fall of water from a higher to a lower level: his directions therefore for the fourth operation (in his order the third, as he started from B) were to compress the body until as much heat has left it as entered.

Dr. Joule having conclusively established the dynamical theory of heat, Professor Clausius¹ first rectified M. Carnot's mistake by directing the compression to be continued so far along the isothermal DA until further compression along an adiabatic would bring the body to state B . We have followed Professor Maxwell's order of the operations, and thus avoided all chance of error and difficulty of expression.

That h cannot be equal to H seems clear from the consideration that, when H is totally transferred from a body at a higher to a body at a lower temperature by conduction, no work is done; thus the circumstances ought to be altered if work is done: and again, if the engine were employed to agitate water, heat would be generated, as Dr. Joule's experiments shew; but this heat would be created out of nothing, were h equal to H . A direct proof of this inequality was first given by M. Hirn's experiments on the steam-engine² in 1854. For each stroke of the piston m grams of vapour leave the boiler at temperature $\Theta^{\circ}\text{C.}$; the boiler being fed with water from the condenser at $\theta^{\circ}\text{C.}$, this vapour according to M. Regnault's experiments absorbs $m\{606.5 + 0.305(\Theta - \theta)\}$ calories from the furnace: thus $H = \mathcal{J}m\{606.5 + 0.305(\Theta - \theta)\}$. To keep the condenser at the constant temperature $\theta^{\circ}\text{C.}$, M grams of water at 3°C. are injected at each stroke and absorb $M(\theta - 3)$ calories; hence $h = \mathcal{J}M(\theta - 3)$. It was always found that H is greater than h ; but to test the correctness of the experiments M. Hirn calculated the heat R lost by radiation and conduction (a very uncertain determination) and the work W done in each stroke.

The latter is the integral $\int_0^l (P - p)\omega dl$, where ω is the area of the piston, l the length of its stroke, P , p the working and resisting pressures on the faces of the piston due respectively to the vapour that has entered the cylinder and the vapour in the condenser, the latter being generally called the *back pressure*: this work is however more conveniently measured by the area of the indicator diagram, or the indicator *card*, as it is technically called.

¹ *Pogg. Ann.* lxxix. (1850) 380, trans. *Phil. Mag.* [4] ii. (1851) 9.

² *Théorie mécanique de la Chaleur*, 3^{ème} éd. (1875), i. 54.

From the equation $H = h + W + R$ he found 40.51 as the mean value of γ : this agrees sufficiently well with Dr. Joule's number, especially considering the difficulty of the experiments.

36. Closed cycles. The general case, wherein the lines of the diagram are any whatever and not merely isothermals and adiabatics, admits of the same treatment. If during change of state from A to B unit mass of the working substance gives up heat H_1 , takes in heat H_2 during the process represented by BC , and H_3 during the process CD , giving up H_4 in its return to A along DA , the work done is represented by the area $ABCD$, and the heat spent in this work is

$$-H_1 + H_2 + H_3 - H_4 = \Sigma H,$$

where H represents heat taken in, being reckoned negative if given out. Thus the most general expression of the first law of thermodynamics for closed cycles is

$$\oint dH = W.$$

A closed cycle is termed *simple* if its bounding curves are of two types only, and *complex* if the curves are any whatever: thus Carnot's cycle is simple, while that of Fig. 12 is complex.

Being given any number of successive operations in each of which the initial and final states are identical, we may always consider them as forming part of one closed cycle. For considering two such series represented by the closed curves $ABCA$, $DEFD$, we may join them by any arbitrary line CD ; then together they differ from the closed cycle $ABCDEFDCA$ only by the operations represented by CD and DC which are exactly inverse to each other in every respect, the difference being thus nothing.

We may also break up any given closed cycle into any number of others by introducing arbitrary operations performed both directly and inversely. Thus the cycle $ABCD$ is

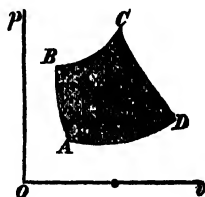


Fig. 12.

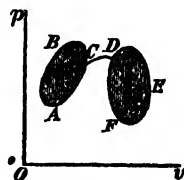


Fig. 13.

equivalent to the two cycles $ABDA$, $BCDB$ together, the arbitrarily introduced operation BD being performed both directly and inversely and having therefore no influence on the whole.

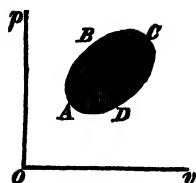


Fig. 14.

37. Reversible engines. A cycle is said to be *reversible* when the indicator diagram is accurately retraced in the opposite direction if the operations are exactly reversed.

Carnot's cycle fulfils this condition; for considering the body initially at B , we may (1) allow it to expand along the adiabatic BA doing work without receiving heat while falling in temperature from T to t , (2) by giving heat h and maintaining its temperature constant bring it to D along the isothermal AD , (3) by compression without loss of heat along the adiabatic DC raise its temperature again to T , (4) by further compression along the isothermal CB restore it to its initial state after taking away heat H . Thus work W , measured by the area $ABCD$, has been done on the body which has on the whole lost heat $H-h$; these being equivalent, we have

$$-(H-h) = \text{area } BADCB = -W,$$

the negative signs denoting *loss* of heat and work done *on* the body. There is this difference only with respect to perfect reversibility: the body is slightly cooler than the source when it receives heat from it as in the direct cycle, but slightly warmer when it gives up heat to it as in the reversed cycle; and similarly it is slightly warmer than the refrigerator in the direct and slightly cooler in the reversed process: if however the expansions and compressions are performed slowly enough, these inequalities may be indefinitely diminished and a perfectly reversible cycle obtained.

We commenced the above process at B instead of A , so as to avoid the difficulty of expression noticed in § 35.

38. Carnot's principle. We have seen that for an engine to supply continuous work, there must be not only a transformation of heat into work but also a transfer of heat from a body at a higher to one at a lower temperature. If W is the work

done when heat H is abstracted from the source, the ratio $\frac{W}{H}$ is termed the *Efficiency* of the engine; and Carnot's Principle is that of all engines with one source and one refrigerator at given constant temperatures the efficiency of a reversible engine is the greatest.

M. Carnot's proof rests on the impossibility of the perpetual motion, *i.e.* of obtaining useful work at no expense of energy: for, on the caloric theory, if any engine A is more efficient than a reversible one R , so that $\frac{W'}{H} > \frac{W}{H}$, or $W' > W$, where W' , W represent the work the engines do respectively while transferring heat H from the same source to the same refrigerator, a balance of useful work $W' - W$ will be obtained without on the whole any transfer of heat when the engines are coupled inversely so that R restores to the source exactly the heat H which A abstracts from it; or the perpetual motion is realized.

Professor Clausius¹ demonstrated in 1850 that this principle still holds good with the dynamical theory of heat: he rests it on the following axiom, not distinctly formulated² till 1854, which he calls the *Second Law of Thermodynamics*:—

Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time; or Heat cannot by itself pass from a colder to a warmer body.

Sir W. Thomson³ in 1851 put this into a more precise form:—*It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.* This latter axiom—the impossibility of getting work by cooling a condenser—seems the safer one to assume on general experimental evidence; the modification of M. Carnot's proof of the above principle required in either case is very slight.

Professor Clausius' modification is the following: if any

¹ *Pogg. Ann.* lxxix. (1850) 500, trans. *Phil. Mag.* [4] ii. (1851) 102.

² *Pogg. Ann.* xciii. (1854) 488, trans. *Phil. Mag.* [4] xii. (1856) 86.

³ *Trans. R. S. E.* xx. (1851) 265, or *Phil. Mag.* [4] iv. (1852) 13.

engine A is more efficient than a reversible one R , so that $\frac{W}{H'} > \frac{W}{H}$, or $H > H'$, where H' , H represent the heat abstracted from the same source by the respective engines to perform the same work W with the same refrigerator, then an amount of heat $H - H'$ will be transferred from the refrigerator to the source without on the whole any expenditure of work when the engines are coupled together inversely so that A just drives R ; and this is contrary to the axiom.

Sir W. Thomson's modification is this: if A is more efficient than R , so that $\frac{W'}{H} > \frac{W}{H}$, or $W' > W$, where W' , W represent the work done by the respective engines with the same refrigerator on abstracting heat H from the source, then an amount of work $W' - W$ will be done without any loss of heat to the source when the engines are coupled inversely, so that R restores to the source exactly the heat H abstracted by A ; this work must therefore have been done at the expense of the heat of the refrigerator, which is contrary to the axiom.

Taken in its strictly literal sense Professor Clausius' axiom—that heat cannot of itself pass from a colder to a hotter body—is perfectly true; thus in Carnot's reversed cycle the working body is just colder than B when it takes in heat and just hotter than A when it gives it out: but it is not strictly correct to call the transference of energy (though taken in by the body as heat and given out as heat) from B to A a transference of heat from a colder to a hotter body, as we know not the form in which the energy exists during the body's adiabatic change of condition. The statement is however intended to assert the impossibility of any such transfer of energy without *compensation*, and this, as Professor Maxwell points out, is only axiomatic if the theory of entropy is so. Professor Maxwell also points out that Sir W. Thomson's axiom requires some restrictions, as by allowing air, compressed in a cylinder at the temperature of the room, to expand we could get work from it though its temperature would fall below that of the coldest of surrounding objects, and that with such restrictions the

axiom would merely re-assert Carnot's principle with greater generality. In fact the second law of thermodynamics is shewn by the kinetic theory of gases not to be true for a group of molecules unless they are sufficient in number to form a sensible part of a body, so that it is a statistical and not a mathematical truth, and therefore not capable of strictly axiomatic statement.

The great importance of Carnot's principle lies in its shewing that all reversible engines have the same efficiency: but reversibility is entirely independent of the working substance of the engine; hence the efficiency of a reversible engine is independent of the working substance and depends only on the temperatures at which heat is taken in and given out. Reversible engines are therefore called *perfect*.

Thus in Carnot's cycle we have

$$\frac{W}{H} = F(T, t);$$

whence, if the difference between the temperatures is infinitely small, or $t = T - dT$,

$$\begin{aligned} \frac{W}{H} &= F(T, T - dT) = F(T, T) - F'(T, T) dT \\ &= -F'(T, T) dT, \end{aligned}$$

since $F(T, T)$ is zero, as no work can be done without a difference of temperature. The quantity $-F'(T, T)$ is called *Carnot's Function*, and is denoted by μ : it is a function of the temperature of the source only.

39. Work in reversible engines of finite range performing Carnot's cycle. By § 36 we may consider a reversible engine of finite range to be made up of an infinite number of reversible engines of infinitesimal range, the refrigerator of each being the source of the next and the heat rejected by one being that which is taken in by the next: for on the whole there is neither loss nor gain of heat except at the limiting temperatures, and the same amount of work is done. If in one of these engines heat H is taken in at temperature T and heat $H - dH$ rejected at temperature $T - dT$, the first law

gives the expression dH , and the second law the expression $\mu H dT$, for the infinitesimal amount of work done. Equating these values we get

$$\frac{dH}{H} = \mu dT. \quad (1)$$

By integration we extend this result over the whole range: thus if T, t are the extreme temperatures, H, h the heat taken in and given out, W the work done,

$$\frac{H}{h} = e^{\int_t^T \mu dT} \quad (2)$$

$$W = H - h = H \left(1 - e^{-\int_t^T \mu dT} \right). \quad (3)$$

This is Sir W. Thomson's general expression¹ for the work done by a reversible engine of finite range performing Carnot's cycle. μ is a function of the temperature which can only be determined by experiment: the best method will be indicated in § 71. But the form of the function will vary with the thermometric scale employed, for, as we have seen, none of the scales in actual use is really absolute. Sir W. Thomson however has made Carnot's theorem the basis of two scales perfectly absolute in the sense of independence of the thermometric substance: these we now give.

ABSOLUTE SCALES OF TEMPERATURE.

40. First absolute scale of temperature. In 1848 Sir W. Thomson² proposed to consider the difference of the temperatures of the source and refrigerator constant when the work done by a perfect engine on abstracting unit heat from the source is constant. Now the work done is by (3) constant when the integral $\int_t^{t+\tau} \mu dt$ is constant, where $t+\tau$ and t are the limiting temperatures; and on the proposed scale this integral will be independent of t and a function of τ only. This requires μ to be constant: for the differential coefficient of the integral with regard to t (which must be zero since the integral is

¹ *Trans. R. S. E.* xx. (1851) 273, or *Phil Mag.* [4] iv. (1852) 106.

² *Phil. Mag.* [3] xxxiii. (1848) 313.

independent of t) is the difference between the values of μ corresponding to the temperatures $t + \tau$ and t , and these values are therefore equal; but τ may be any quantity whatever, so that μ must be the same for all temperatures.

In this case therefore equation (3) becomes

$$\frac{W}{H} = 1 - e^{-\mu\tau} = 1 - a^{\tau},$$

if $e^{-\mu} = a$; also equation (2) becomes

$$\frac{H}{h} = e^{\mu\tau} = b^{\tau},$$

if we write $b = e^{\mu} = \frac{1}{a}$. As therefore the difference in temperature of the source and refrigerator of a perfect engine changes in arithmetical progression, the ratio of the amounts of heat taken from the source and given to the refrigerator changes in geometrical progression.

It is found by experiment, indicated in the next article, that the efficiency of a perfect engine working between 0° and 100°C . is $\frac{100}{373.7}$: hence if we consider these temperatures the arbitrary points which coincide on the absolute and centigrade scales, we have

$$a^{100} = 1 - \frac{100}{373.7} = 0.73241,$$

and therefore $a = 0.99689$, $b = 1.00312$, $\mu = 0.003114$.

This scale is found to differ very greatly from that of the air thermometer, more and more degrees of the latter going to one of the former as the temperature rises: and again, the absolute zero of temperature on this scale is $-\infty$; for, were it the temperature of the refrigerator, $h = 0$ (as all bodies absolutely cold are entirely deprived of heat), and therefore τ is infinite, or absolute zero is infinitely below any finite temperature that a source may have. On both accounts then this scale is very inconvenient and has therefore yielded to another absolute system.

41. Second absolute scale of temperature. In 1845 M. Holtzmann, starting from incorrect principles, concluded that μ is inversely as the temperature from zero on the air-thermometer, and in 1850 Professor Clausius arrived at the

same conclusion by applying his amended form of Carnot's principle to the case of gases in a hypothetical perfect state. But this scale is not strictly absolute, as it depends on the state of the gas used and does not rest entirely on thermodynamic principles: defining temperatures however with Sir W. Thomson¹ so that Carnot's function at any temperature is the reciprocal of that temperature we obtain a scale that is perfectly absolute. This definition moreover appears natural; 'for in equation (1), as temperature is a definite magnitude, homogeneity requires μ to be the reciprocal of a linear function of T . Taking then $\mu = \frac{1}{T}$, we transform equations (2) and (3) into

$$\frac{H}{h} = \frac{T}{t}, \quad (4)$$

and

$$\frac{W}{H} = \frac{T-t}{T}. \quad (5)$$

Hence Sir W. Thomson remarks² that 'the absolute values of two temperatures are to one another in the proportion of the heat taken in to the heat rejected in a perfect thermodynamic engine working with a source and refrigerator at the higher and lower of the temperatures respectively.'

This scale admits of a very elegant graphical expression. Draw the isothermal for any temperature T , and let A represent

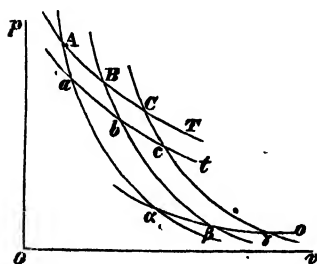


Fig. 15.

the initial state of unit mass of the working substance of a perfect engine, B, C, \dots its successive states after communication of heat $H, 2H, \dots$ at the constant temperature T . Through A, B, C, \dots draw the adiabatics Aa, Bb, Cc, \dots ; if any other isothermal as $abc \dots$ is drawn, the areas $ABbaA, BCcbB, \dots$ will all be equal, as they measure the

work done by perfect engines working between the same tem-

¹ *Phil. Trans.* cxliv. (1854) 351.

² *Trans. R. S. E.* xxi. (1854) 125, or *Phil. Mag.* [4] xi. (1856) 216.

peratures and abstracting the same amounts of heat from the source. Draw the isothermal $a\beta\gamma \dots$ corresponding to total deprivation of heat or to absolute zero temperature; if this is the temperature of the refrigerator, the whole of the heat H taken in at T is transformed into work, or the areas $AB\beta aA$, $BC\gamma\beta B$, \dots are all equal to H . Divide these areas into T equal parts by a series of isothermals, each part being therefore $\frac{H}{T}$:

then Sir W. Thomson's scale of absolute temperatures is given by these successive isothermals. If $abc \dots$ is the isothermal corresponding to temperature t , there are $T-t$ of these small areas in $ABbaA$, or $ABbaA = H \frac{T-t}{T}$: now $ABbaA$ is the work done by a perfect engine working between T and t and taking in heat H at the higher temperature; its efficiency is therefore

$$\frac{W}{H} = \frac{T-t}{T},$$

the expression found before.

Professor Rankine¹ arrived in 1851 at a similar expression in terms of the absolute temperatures on the air-thermometer, deriving it directly from the first law—without assuming a second—on his peculiar hypothesis of molecular vortices.

Thus far the degrees of the new scale are arbitrary: it is convenient to determine them by drawing the isothermals for 0°C. and 100°C. , dividing the area between these lines and consecutive adiabatics into 100 equal parts, and taking one of these parts as unit area, or area between consecutive isothermals. Then if the area $AB\beta aA$ contains T such areas, the isothermal AB is that for temperature T .

Experiment shews that the absolute zero temperature is about -273.72°C. ; the reason of the approximate coincidence of this zero with that of the air-thermometer, which suggested the scale, will appear in § 71, where the method of experiment will be described.

It is best to draw the adiabatics so that the area included

¹ *Trans. R. S. E.* xx. (1851) 208.

between consecutive adiabatics and isothermals represents unit work. This area being $\frac{H}{T}$, H must be taken numerically equal to T , and then consecutive adiabatics are defined by a series of points A, B, C, \dots on the isothermal for T , which represent the successive states of unit mass of the working substance of a perfect engine after successive additions of T megalergs of heat at the constant temperature T . The adiabatics may be numbered $0, 1, 2, \dots, \phi$, beginning with the line of no heat: then if a perfect engine work between the isothermals t, t_0 and the adiabatics ϕ, ϕ_0 , the total work done is $(t - t_0)(\phi - \phi_0)$.

The signification of ϕ is given in § 60; it is really the *entropy* of the body.

In future, the next article excepted, we shall always denote absolute temperature by t , temperature on the Centigrade scale by θ , and absolute temperature on the air-thermometer by τ : in all three scales 100 degrees occur between the temperatures of melting ice and boiling water.

42. Comparison of the two absolute thermometric scales. To shew the disadvantage of the absolute scale first proposed we subjoin a table of simultaneous temperatures on

$T - 273.7$	T	T'	$T - 273.7$	T	T'
-273.7	0.0	- ∞	150	423.7	140.3
250	23.7	785.6	200	473.7	176.1
200	73.7	421.3	250	523.7	208.4
150	123.7	255.0	300	573.7	237.6
100	173.7	146.0	350	623.7	264.5
50	223.7	64.8	400	673.7	289.2
0	273.7	0.0	450	723.7	312.2
+ 50	323.7	+ 53.9	500	773.7	333.7
100	373.7	100.0			

the different scales, supposing that in both the temperature of boiling water is higher by 100 degrees than that of melting ice when the pressure is normal. T' represents temperature according to the first scale, and T according to the second; the first column gives the readings of the second scale if the tem-

perature of melting ice is taken as its zero. The comparison is easily made; for

$$\frac{T}{t} = \frac{H}{h} = \frac{\delta T}{\delta t},$$

and at the temperature of melting ice $t = 273.7$, $t' = 0$; hence

$$T = 273.7 \delta T',$$

$$T' = \frac{\log T - \log 273.7}{\log 1.00312} = 739.3715 \log T - 1802.05.$$

43. Zero thermal lines. We know absolutely nothing about the properties of solids at very low temperatures, but we can easily see to what results §§ 27, 28 will lead. The stress exerted by a body, being the result of the motion of its atoms, is zero only when they are at rest, which occurs when the temperature also is zero: hence the zero isopiestic and the zero isothermal coincide. But to $p = 0$, $t = 0$ can correspond only a single value of v , which must be the minimum volume that unit mass can occupy, since otherwise the atoms would begin to move under their mutual attractions and so to exert stress; the zero isopiestic or isothermal thus reduce to the point which characterizes this limiting state of the body. Again, as the temperature of a body in which there is no heat is always zero, the zero adiabatic coincides with the zero isothermal, and so also does the zero isenergetic by §.32: they are therefore also represented by the point that characterizes the state of the body when absolutely cold. Zero isometric there is obviously none, for the body cannot be squeezed into nothing.

As no two real adiabatics cut each other, so no real adiabatic cuts the real zero isothermal, which is a real adiabatic; hence no adiabatic cuts the zero isothermal, and thus it would be impossible to construct Fig. 15 exactly as is described: we might however substitute for the zero isothermal that part of the axis of v (infinitely distant from the axis of co-ordinates) which is asymptotic to the adiabatics.

Professor Maxwell¹ ingeniously avoids the infinite diagram given by this method—and at the same time all hypotheses

¹ *Theory of Heat*, 4th ed. (1875), 164.

as to the state of the bodies at temperatures beyond the reach of experiment—by employing a fictitious zero isothermal and a series of fictitious adiabatics.

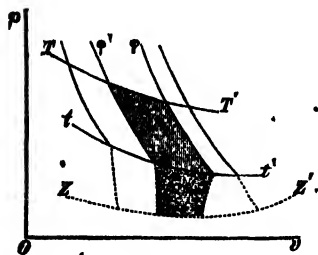


Fig. 16.

Thus if the isothermal tt' corresponding to temperature t bounds the part of the diagram that is known by experiment, and the adiabatics that cut it are continued by lines that do not intersect each other, then the line ZZ' , which is drawn so that the area included between it, the

isothermal tt' , and the continuations of any two adiabatics ϕ and ϕ' , is equal to $t(\phi - \phi')$, may be treated as the zero isothermal and the prolonged lines as adiabatics. For the area included between the adiabatics ϕ and ϕ' , the isothermal tt' , and any other isothermal TT' corresponding to temperature T in the known part of the diagram, is $(T - t)(\phi - \phi')$, and the continuation of this area is $t(\phi - \phi')$, so that the whole area included between the lines TT' , ZZ' , and the adiabatics ϕ , ϕ' with their continuations, is $T(\phi - \phi')$, and it therefore represents the heat taken in by a body when it passes from the adiabatic ϕ' to the adiabatic ϕ at the constant temperature T .

44. Intersection of thermal lines. M. Verdet¹ maintains that two adiabatics cannot intersect, and offers as proof the following:—if AC, BC are two adiabatics that intersect in C , a body, after traversing the isothermal AB and receiving heat therein, can traverse the adiabatics, doing work equal to $ABCA$ without any accompanying transfer of heat; and this is impossible. This proof is fallacious; for Professor Rücker,² has pointed out that it is impossible for the body to pass at the point C from one

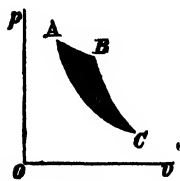


Fig. 17.

¹ *Théorie mécanique de la Chaleur* (1868), i. 184.

² *Proc. R. S.* xxii. (1874) 452.

adiabatic to the other without absorbing or emitting heat, i. e. while fulfilling the very condition that it should *not* pass from one adiabatic to another. He has further shewn that this proposition is true only if the temperature is perfectly defined when the pressure and density are given. A single instance—the most striking case—of the intersection of adiabatics will make this clear.

At ordinary atmospheric pressure denoted by the dotted isopiestic in the diagram let *A*. and *B* represent the state of unit mass of water at the temperatures 0°C . and 4°C . respectively: starting from any initial condition *P* between these two states at a temperature below 4°C ., the body will contract on absorbing heat at constant pressure till it reaches *B*, where its density is maximum: further addition of heat will cause it to repass through the same states of density as before, but at different temperatures.

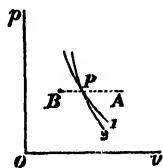


Fig. 18.

On regaining the density represented by *P*, it will now possess in addition to its initial stock of heat all that has been supplied; for none has been expended in work, the contraction and expansion having exactly compensated each other: hence each point *P* between *A* and *B* may be regarded as on two adiabatics, which there intersect.

This case is even more striking; for if we cool the water still at the constant pressure, until it freezes,—in which case its volume becomes greater than that denoted by *A*,—and then continue the abstraction of heat, we may reduce its volume again to that of the initial state *P*; this state must therefore correspond to a third adiabatic through *P*, as on the whole no work is done while the heat is abstracted. Thus three adiabatics pass through every point between those corresponding to 0°C . and 4°C ., and, the case being similar on the neighbouring isopiestic, there is a region in the plane of *pv* each point of which corresponds to three different states of the water-substance: hence not only do three adiabatics intersect at each point in this region, but there also pass through it three

isothermals, three isenergics, in short, three thermal lines of every type except isopiestic and isometrics.

Such points of intersection of thermal lines are not the projections of real intersections of the corresponding real thermal lines, but denote that these curves in space seem to cross each other when viewed from the plane of pv : Professor Rücker therefore proposes to reserve the usual terms (intersect, cut, meet, &c.) for the projections of curves that actually meet on the characteristic surface, and to use the term *cross* for the projections, which intersect, of curves that do not meet in space.

There are some peculiarities in the thermal lines in this region wherein all crossings occur, which Professor Rücker has also pointed out. It is an experimental fact, upon which we shall say more in § 78, that a substance which would contract on absorbing heat under constant pressure, such as water between 0° and 4°C ., experiences a rise in temperature when allowed to expand without receiving or emitting heat; this rise however cannot go on indefinitely, as work is done at the expense of the intrinsic energy which is finally due (see § 63) to the temperature increased only by a constant quantity (the potential energy of infinite molecular separation): hence on the real adiabat through the point representing the initial state—and all such points—there must be a point of maximum temperature, and the real isothermals through all other points of the same curve which lie within this region must meet it twice. Now the condition

$$\frac{\partial f}{\partial t} = 0.$$

coupled with the equation to the characteristic surface

$$f(p, v, t) = 0$$

gives the locus of the points of maximum temperature, and this curve therefore bounds the region in which real adiabatics are cut twice by the same real isothermal, and its projection on the plane of pv bounds the region in which two isothermals or any two thermal lines of the same type can cross each other. Also, since at all points on the curve of maximum temperature the tangent planes to the surface are perpendicular to the plane of

pv , the projections on that plane of all lines meeting it touch its projection.

Again, the projections of a real adiabetic and a real isothermal that meet twice also meet in two points, say A and B : they must further *cross* each other at some intermediate point C , and thus form two loops, since the adiabetic at a point is (§ 33) always steeper than the isothermal. The isothermal that corresponds at C to this adiabetic will of course be represented by some such line as the dotted one, which conforms to the same rule. These three points coincide in the limiting case where the adiabetic meets the isothermal corresponding to the maximum temperature above mentioned (that is, at the point where it touches the bounding curve of the region), and there is therefore contact of the second order between these lines.

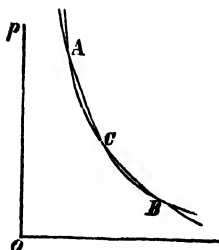


Fig. 19.

Consider (Fig. 20) a pair of isothermals $ABCD$, $D'C'B'A'$, each cutting twice a pair of adiabatics $BC'B'C$, $AD'A'D$, and let the different lines further cross each other in the points O , O' , P , Q , R , S , as in the diagram: they all have contact of at least the second order with the line which is the projection of the curve of maximum temperature. Between the temperatures corresponding to these isothermals we can make the substance under consideration perform Carnot's cycle in twelve different ways.

(i) Giving or removing the same amount of heat along AB , we can make the body traverse either the cycle $ABC'D'A$ or the cycle $ABB'A'A$; these areas are therefore equal, and their difference, the area $C'OB'A'OD'C'$, is zero, or the two areas $OA'B'O$, $OD'C'O$, which are traversed in opposite directions, are equal. Or again, giving or removing the same amount of heat along $A'B'$, we can allow either the cycle $A'B'CDA'$ or the cycle $A'B'BAA'$ to be traversed; these areas (regard being paid to their sign) are therefore equal, and their difference, the area

$CDOABOC$, is zero, or the areas $OABO$; $ODCO$, which are traversed in opposite directions, are equal. Hence *the areas of the two loops formed by two adiabatics and an isothermal which meets each of them twice are equal.*

(ii) Similarly, if we consider either of the pairs of equal cycles

$$\left. \begin{array}{l} ACC'A'A \\ ACB'A'A \end{array} \right\} \left. \begin{array}{l} ACC'D'A \\ ACB'D'A \end{array} \right\},$$

we find that the area $B'O'PC'OPB'$ is zero, or the areas $PO'B'P$, $PC'OP$ are equal; and these equal cycles, paired together differently as

$$\left. \begin{array}{l} ACC'A'A \\ ACC'D'A \end{array} \right\} \text{ or } \left. \begin{array}{l} ACB'A'A \\ ACB'D'A \end{array} \right\},$$

shew that the area $D'OQA'O'QD'$ is zero, or the areas $QOD'Q$, $QA'O'Q$ equal. Or again, of the four equal cycles $A'C'CAA'$, $A'C'CDA'$, $A'C'BAA'$, $A'C'BDA'$ either of the pairs

$$\left. \begin{array}{l} A'C'CAA' \\ A'C'BAA' \end{array} \right\} \left. \begin{array}{l} A'C'CDA' \\ A'C'BDA' \end{array} \right\}$$

gives the area $BORCO'RB$ zero, or the areas $ROBR$, $RCO'R$ equal, and either of the pairs

$$\left. \begin{array}{l} A'C'CAA' \\ A'C'CDA' \end{array} \right\} \text{ or } \left. \begin{array}{l} A'C'BAA' \\ A'C'BDA' \end{array} \right\}$$

gives the area $DO'SAOSD$ zero, or the areas $SOAS$, $SDO'S$ equal. Thus *the areas of the loops formed by any adiabatic and an isothermal which meets it twice are equal.*

This latter result may be deduced from the former by supposing the two points of intersection of one of the adiabatics with the isothermal to coincide. We see therefore that, *if a body perform a cycle of operations which can be represented by an adiabatic and an isothermal, it will on the whole do no useful work.*

From the above the areas $ROBR$, $RCO'R$ are equal, and by adding to each the area $O'PRO'$ we see that the areas $O'POBO'$, $O'PCO'$ are equal; if now we subtract from these respectively the equal areas $POC'P$, $PB'O'P$, we find that the areas $O'C'BO'$, $O'B'CO'$ are also equal: hence the further proposition:—*the areas of the two loops formed by two isothermals and an adiabatic which meets each of them twice are equal.*

Similar results are obtained on considering the shapes of the thermal lines near their other intersections with the boundary line of the anomalous region where it corresponds for any given pressure to a local maximum volume: but in the case of water the considerations are more complicated by reason of discontinuity occurring in the thermal lines. Hence the real isothermals that pass through all the points of a real adiabatic that lie between the two points where it touches the boundary line of this region—the points of local maximum and minimum temperatures—meet it in *three* points: the same is true of the projections of these curves, but, as an adiabatic is always steeper than an isothermal at their point of intersection, the lines must further cross in *two* points intermediate to the points of intersection, and there are thus formed four loops which by the above proposition are equal, two and two.

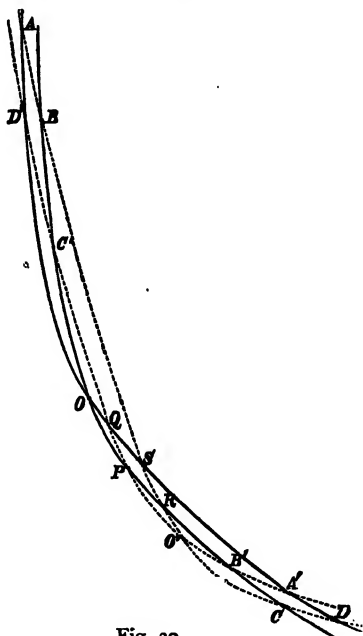


Fig. 20.

SECOND LAW OF THERMODYNAMICS.

45. Generalization of Carnot's principle. To Sir W. Thomson¹ is due the following extension and generalization of the results of Carnot's principle:—if H represents the heat taken in or given out at the absolute temperature T , being considered negative if given out, by a perfect engine with several

¹ *Trans. R. S. E.* xxi. (1854) 126, or *Phil. Mag.* [4] xi (1856) 217.

sources and refrigerators at different temperatures, then the sum of all the quantities $\frac{H}{T}$ is zero, or

$$\sum \frac{H}{T} = 0.$$

This is obviously true for Carnot's simple cycle; for we have $\frac{H}{T} - \frac{h}{t} = 0$. Consider now, with Professor Zeuner¹, a cycle with two sources at temperatures T_1 , T_2 wherefrom amounts of heat H_1 , H_2 are taken, and a refrigerator at temperature t to which heat h is given out, the diagram being composed of is-

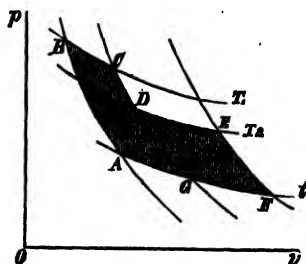


Fig. 21.

thermals and adiabatics. Let the initial state of unit mass of the working substance of the engine at temperature t be denoted by A : (1) compression without loss of heat till the temperature rises to T_1 brings the mass along the adiabat to B ; (2) heat H_1 given at the constant temperature T_1 takes it along the isothermal to C ; (3) further expansion without

gain of heat till the temperature falls to T_2 carries it along the adiabat to D ; (4) communication of heat H_2 at the constant temperature T_2 moves it along the isothermal to E ; (5) a final expansion without gain of heat till the temperature falls to t takes it along the adiabat to F ; (6) a final compression at the constant temperature t with loss of heat h brings it back to its initial state A . This process is obviously reversible. If the adiabat CD intersects the isothermal FA in G , and h is composed of heat h'' emitted along FG and h' emitted along GA , the complete cycle may be considered as made up of the two simple cycles $ABCGA$, $DEFGD$; hence we have

$$\frac{H_1}{T_1} - \frac{h'}{t} = 0 \quad \text{and} \quad \frac{H_2}{T_2} - \frac{h''}{t} = 0,$$

¹ *Grundzüge der mechanischen Wärmetheorie*, 2^{te} Aufl. (1877), 62.

whence on addition

$$\frac{H_1}{T_1} + \frac{H_2}{T_2} - \frac{h}{t} \equiv \sum \frac{H}{T} = 0.$$

The same method may be applied whatever the number of sources and refrigerators and however complicated the diagram provided that it is composed of isothermals and adiabatics.

The following proof is general for this case. Suppose the quantities of heat $H_1, H_2, \dots H_n$ are taken in at temperatures $T_1, T_2, \dots T_n$ respectively, a negative value of H denoting emission; add a perfect engine emitting H_1 at T_1 and taking in $\mathfrak{C} \frac{H_1}{T_1}$ at \mathfrak{C} , another emitting H_2 at T_2 and taking in $\mathfrak{C} \frac{H_2}{T_2}$ at \mathfrak{C} , and so on: these n perfect engines together with the given one emit on the whole no heat, but take in

$$\mathfrak{C} \left(\frac{H_1}{T_1} + \frac{H_2}{T_2} + \dots + \frac{H_n}{T_n} \right);$$

this quantity must however be zero, for, whenever heat is taken in by an engine, part of it is emitted since the whole of it cannot be converted into work; hence

$$\frac{H_1}{T_1} + \frac{H_2}{T_2} + \dots + \frac{H_n}{T_n} \equiv \sum \frac{H}{T} = 0.$$

If the adiabatics come close together, the summation becomes integration, and

$$\int \frac{dH}{T} = 0.$$

In the case of a continuous cycle-curve, divide the diagram into an infinite number of cycles by adiabatics infinitely near each other and consider one of them $PQRSP$, in which dH is taken in along PQ at T and dh given out along RS at t : draw the isothermals that pass through P and R . Then we may consider the cycle $PQRS$ as composed of the three cycles $PQQ'P$, $PQ'RS'P$, $S'RSS'$; but in the cycle $PQQ'P$ the difference between the

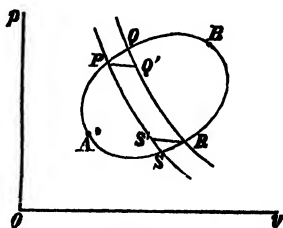


Fig. 22.

heat taken in and the heat emitted is negligible, being measured by the area $PQQ'P$ which is an infinitesimal of the second order, and the same is the case with $S'RSS'$; hence Carnot's cycle $PQ'RS'P$ (whose area is an infinitesimal of the first order only) may be considered as taking in dH at T and giving out dh at t , and therefore

$$\frac{dH}{T} - \frac{dh}{t} = 0,$$

or on integration over the whole cycle

$$\int \frac{dH}{T} = 0. \quad (6)$$

If we take the integrals between any two points A and B , we have

$$\int_A^B \frac{dH}{T} + \int_B^A \frac{dH}{T} = 0,$$

where the first integral refers to the part $APQB$ of the curve and the second to the part $BRSA$: if then we keep the first part constant but vary the second in any way, still keeping the whole cycle reversible, the value of the integral $\int_B^A \frac{dH}{T}$ remains always the same: the integral therefore depends only upon its limits, or $\frac{dH}{T}$ is a perfect differential in reversible cycles.

The above generalization of Carnot's principle we may consider as the second law of thermodynamics. Thus the two laws with respect to the absorption and transformation of heat in closed reversible cycles are expressed by

$$\int dH = W,$$

$$\int \frac{dH}{T} = 0.$$

46. Equivalence of transformations. Professor Clausius¹ has established the above equation (6) by a very different course of reasoning, and has given it a physical meaning.

M. Carnot's theorem may be stated thus:—Whenever a quantity of heat is converted into work by a reversible process and the substance effecting this transformation passes through

¹ *Pogg. Ann.* xciii. (1854) 481, trans. *Phil. Mag.* [4] xii. (1856) 81.

a complete cycle of changes, another quantity of heat must be transmitted from a warmer to a colder body; and the relation between these quantities depends only on the temperatures. The real law of dependence of this relation on the temperatures is not brought into view by the simple cycle proposed by M. Carnot; for the heat transmitted is taken therein at the same temperature as that transformed. The following cycle suggested by Professor Clausius is more general.

Let unit-mass of any substance, enclosed in a piston-fitted cylinder, be at temperature T , and be represented as to pressure and volume in its initial state by the position A on the diagram: (1) expansion without gain of heat till the temperature falls to T_1 brings it along the adiabatic to B :

(2) then communication of heat h at the constant temperature T_1 moves it along the isothermal to C :

(3) a further expansion without gain of heat till its temperature becomes T_2 brings it hence along the adiabatic to D : (4) compression now at the constant temperature T_2 until all the communicated heat h is given up moves it along the isothermal to E :

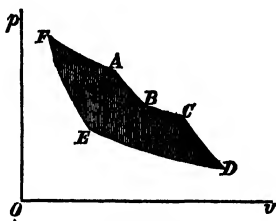


Fig. 23.

(5) a further compression without loss of heat till its temperature rises to T changes its state along the adiabatic to F , where its volume is smaller than at A ; for otherwise, as F is on the isothermal AF , the line EF would cut one of the lines already traced, and work represented by the area so enclosed would have been done without on the whole any expenditure of heat: (6) communication of heat H at the constant temperature T brings it back along the isothermal to its original condition A . In this cycle, then, heat H at temperature T is transformed into work, while also heat h is transferred from a body at the higher temperature T_1 to one at the lower T_2 .

This cycle is reversible, and the relation between H , and h depends only on the temperatures; for were two engines performing such cycles in which H , T , T_1 , T_2 are the same but

h different, coupled together with that one reversed wherein h is the greater, then on the whole, without any other change, heat equal to the excess of the larger value of h over the smaller would be transformed from the lower to the higher temperature—which contradicts the fundamental axiom.

Heat naturally tends to equalize differences of temperature, that is, to pass from warmer to colder bodies; and Clausius' cycle shews that 'a passage in the contrary direction can only take place under circumstances where simultaneously another quantity of heat passes from a warmer to a colder body, or when some change occurs which has the peculiarity of not being reversible without causing on its part such a transfer from a warmer to a colder body¹.' Two transformations, one of which must accompany the passage of heat from a body at one temperature to a body at another, may be considered as *equivalent*: thus from the above cycle reversed the transformation of work into heat H at temperature T is equivalent to the transformation of heat h from the higher temperature T_1 to the lower T_2 , and these are considered *negative* transformations; similarly the transformation into work of heat H at temperature T is equivalent to the transformation of heat h from the lower temperature T_2 to the higher T_1 , these being *positive* transformations. We have here reversed Professor Clausius' convention of signs (as he himself did later²) for agreement with that already assumed.

Every transformation must therefore be measurable, or have an *equivalence-value*. If $\frac{H}{\mathfrak{X}}$ is that of a transformation into work of heat H at temperature T , \mathfrak{X} being a certain function of T , and $H\psi(T_1, T_2)$ that of a transformation of heat H from temperature T_1 to temperature T_2 , consideration of the above cycle gives

$$\frac{H}{\mathfrak{X}} = h\psi(T_2, T_1).$$

Another similar cycle, wherein h , T_1 , T_2 are unchanged but H and T replaced by H' and T' , will give

$$\frac{H'}{\mathfrak{X}'} = h\psi(T_2, T_1).$$

¹ Pogg. Ann. cxx. (1863) 430.

² Pogg. Ann. cxxv. (1865) 356.

Suppose T greater than T' , and let the second cycle reversed be coupled to the first: then, as h is transformed both from T_1 to T_2 and from T_2 to T_1 , the total result is work performed while heat H is taken in at T and heat H' given out at T' , i.e. the transformation into work of heat $H-H'$ at temperature T together with the transformation of heat H' from the temperature T to the temperature T' ; therefore

$$\frac{H-H'}{\mathfrak{X}} = H' \psi(T', T).$$

On eliminating H, H' by the above equations, we find

$$\psi(T', T) = \frac{1}{\mathfrak{X}'} - \frac{1}{\mathfrak{X}}.$$

Hence the second fundamental theorem, which is in this form fitly called *the theorem of the equivalence of transformations*, may be thus enunciated:—*If two transformations, one of which must accompany a third transformation, are called equivalent, then a transformation into work of heat H at the temperature T has the equivalence-value $\frac{H}{\mathfrak{X}}$, and a transformation of heat H from temperature T_1 to temperature T_2 has the equivalence-value $H(\frac{1}{\mathfrak{X}_1} - \frac{1}{\mathfrak{X}_2})$, wherein \mathfrak{X} is a function of the temperature entirely independent of the process by which the transformation is effected.*

Thus the equivalence-value of a transformation of the second kind is equal to the difference between those of two transformations of the first kind, and we can therefore prove in the most general case that *the algebraic sum of the equivalence-values of all the transformations occurring in a reversible cycle is zero*. For the transformations may be all considered as composed of transformations of the first kind, that is, of heat into work, thus giving a series of equivalence-values $\frac{H_1}{\mathfrak{X}_1}, \frac{H_2}{\mathfrak{X}_2}, \dots$; and each of these latter is equivalent to a transformation of the second kind between two given temperatures T, T_0 , so that

$$\frac{H_1}{\mathfrak{X}_1} = h_1 \left(\frac{1}{\mathfrak{X}_0} - \frac{1}{\mathfrak{X}} \right), \quad \frac{H_2}{\mathfrak{X}_2} = h_2 \left(\frac{1}{\mathfrak{X}_0} - \frac{1}{\mathfrak{X}} \right), \dots;$$

hence the transformations are together equivalent to a trans-

formation of heat $\mathfrak{h}_1 + \mathfrak{h}_2 + \dots \equiv \mathfrak{h}$ from the lower temperature T_0 to the higher T : now if \mathfrak{h} is positive, this gives a passage of heat from a lower to a higher temperature without any other compensating change—which is contrary to the fundamental axiom; and if \mathfrak{h} is negative, a reversal of the cycle will make it positive and reduce this to the foregoing impossible case: \mathfrak{h} is therefore zero.

Hence the mathematical expression of this law for reversible cycles is

$$\sum \frac{H}{\mathfrak{T}} = 0,$$

or more generally

$$\int \frac{dH}{\mathfrak{T}} = 0,$$

where dH represents the heat taken in at temperature T , being reckoned negative if it is given out.

By assuming that no heat is absorbed by permanent gases in internal work when changing state, Professor Clausius finds that \mathfrak{T} is proportional to the absolute temperature on the air-thermometer. This suggests taking \mathfrak{T} as absolute temperature without reference to any thermometric scale or any substance, and the above results then become those deduced somewhat earlier by Sir W. Thomson.

47. Reversible cycles not closed.

Let A, B, C represent the successive states of a body in an open cycle: as $\frac{dH}{T}$ is a perfect differential ($d\phi$ say), its integral along the path AC

$$\int_A^C \frac{dH}{T} = \phi_C - \phi_A. \quad (7)$$

The physical meaning of ϕ is given in § 60.

The value of this integral may be exhibited graphically. Let the isothermal through A meet the adiabatic through C in D ; then, the path ABC being reversible, the whole cycle $ABCD A$ is reversible, and the integral over the whole cycle

$$\int \frac{dH}{T} \equiv \int_A^C \frac{dH}{T} + \int_C^D \frac{dH}{T} + \int_D^A \frac{dH}{T} = 0;$$

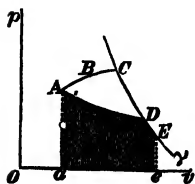


Fig. 24.

but $\int_C^D \frac{dH}{T}$ is zero, as CD is an adiabatic, and $\int_D^A \frac{dH}{T}$ is $-\frac{h}{t}$, if h is the heat required to bring the body from A to D along AD which is the isothermal for t : therefore

$$\int_A^C \frac{dH}{T} = \frac{h}{t}.$$

But, by § 33, h is the area $ADEaA$, where E is the intersection of the isenergetic through A with the adiabatic through C ; thus the value of the integral is the t^{th} part of this area.

48. Mathematical expression of Carnot's principle. Consider an infinitesimally small cycle $ABCD$ formed of the adiabatics AB , CD and the isothermals BC , DA for the temperatures t , $t - \delta t$. Draw the ordinates Bb , Cc , and produce DA to F . The heat given along the isothermal BC in the notation of § 15 is $l \times \overline{bc} = l \delta v$; and the area $ABCD$, which measures the work done, may be considered a parallelogram and therefore equal to $BCEFB$ or $BF \times bc$; but BF is the increase of pressure at constant volume due to the increase δt of temperature, or $\frac{\partial p}{\partial t} \delta t$;

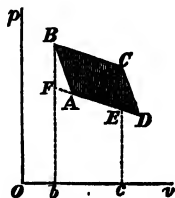


Fig. 25.

hence by (1)

$$\frac{\frac{\partial p}{\partial t} \delta t \delta v}{l \delta v} = \mu \delta t$$

or
$$\frac{\partial p}{\partial t} = \mu l.$$

In this form it was first given by M. Clapeyron¹: with the convention of § 41 this becomes

$$\frac{\partial p}{\partial t} = \frac{l}{t}. \quad (8)$$

49. Dr. Zeuner's method. From the difficulty of giving a precise mathematical definition of temperature and from a desire to derive, if possible, all thermodynamics from the first law only, Dr. Zeuner² has proceeded by another method. Since the state of a body is completely defined in general by its density

¹ *Journ. de l'Ecole Poly.* xiv. (1834) 153.

² *Grundzüge der mechanischen Wärmetheorie* (1877), 39 et seq.

and pressure, E may be expressed as a function of p and v , and the general equation (2) of § 31 may therefore be written

$$dH = p dp + v dv,$$

where $p = \frac{\partial E}{\partial p}$ and $v = \frac{\partial E}{\partial v} + p$:

from these we have on partial differentiation and subtraction

$$\frac{\partial v}{\partial p} - \frac{\partial p}{\partial v} = 1. \quad (9)$$

This may be called the first fundamental equation, and it shews that dH is not a perfect differential.

Let $\frac{1}{\tau}$ therefore be an integrating factor; then $\frac{dH}{\tau}$ being a perfect differential,

$$\frac{\partial}{\partial p} \cdot \frac{v}{\tau} = \frac{\partial}{\partial v} \cdot \frac{p}{\tau},$$

whence on differentiation and simplification by (9) we find

$$\tau = v \frac{\partial \tau}{\partial p} - p \frac{\partial \tau}{\partial v}. \quad (10)$$

This equation, which may be called the second fundamental equation, was first given by M. Clapeyron¹, whose reasoning and method were of entirely different character.

Using the value of v given by equation (10), we have

$$\begin{aligned} p dp + v dv &= p dp + \frac{1}{\frac{\partial \tau}{\partial p}} \left(\tau + p \frac{\partial \tau}{\partial v} \right) dv \\ &= \frac{1}{\frac{\partial \tau}{\partial p}} (p d\tau + \tau dv). \end{aligned}$$

Hence the general equation may be written

$$\left. \begin{aligned} dH &= p dp + v dv, \\ &= \frac{1}{\frac{\partial \tau}{\partial p}} (p d\tau + \tau dv) \\ &= \frac{1}{\frac{\partial \tau}{\partial v}} (v d\tau - \tau dp) \end{aligned} \right\} \quad (11)$$

according to the variables we wish to take.

¹ *Journ. de l'Ecole Poly.* xiv. (1834) 153.

If now we consider a cycle represented by two adiabatics and two lines defined by $\tau = \text{const.}$, $\tau' = \text{const.}$ respectively, then, as τ is so defined that for *all* closed reversible cycles

$$\int \frac{dH}{\tau} = 0,$$

we have

$$\frac{H}{\tau} = \frac{H'}{\tau'}, \quad (12)$$

$$W \equiv H - H' = \frac{H}{\tau} (\tau - \tau'), \quad (13)$$

where W is the work done when heat H is taken in along the line $\tau = \text{const.}$, and heat H' given out along the line $\tau' = \text{const.}$

Now if a mass m be lifted from a level A through a height h to a level B at a spot where its weight is w , the work done against gravitation is

$$w = wh;$$

and if the mass is raised only through a height h' to the level C , the work done is

$$w' = wh';$$

whence

$$\frac{w}{h} = \frac{w'}{h'}. \quad (14)$$

Again, if the mass is raised from level C to level B , the work done is

$$W = w - w' = \frac{w}{h} (h - h'), \quad (15)$$

and this process is reversible; for, if the mass is allowed to sink slowly from the higher level to the lower and do work, the work it does is given by the same equation.

As H , being heat, is work, there is a perfect likeness between equations (12), (13) and (14), (15): τ is thus analogous to a height and $\frac{H}{\tau}$ to a weight, whence Dr. Zeuner calls them a *thermic height* and *thermic weight* respectively; and the above cyclical process may be looked on as the transference of a thermic weight $\frac{H}{\tau}$ from the level τ to the level τ' . Equation (15) however gives the *minimum* amount of work required to raise the mass m through the height $h - h'$, or the *maximum* amount of work that the mass can do in sinking through

this height—i.e. when the velocity on reaching the new levels is infinitely small; furthermore it is impossible for the mass to rise without the expenditure of work: hence, if the above analogy holds, (1) the work done in the cycle when the thermic weight $\frac{H}{\tau}$ is let down from the level τ to the level τ' is a maximum; (2) during this transfer under other conditions less work may be done; (3) the transfer from the lower to the higher level cannot occur without the expenditure of work, which is at least equal to $\frac{H}{\tau}(\tau - \tau')$. Now we know by experience that we can gain work when heat is allowed to pass from a body at a higher temperature to one at a lower (e.g. in the steam-engine from the furnace to the condenser), that this work is the less the more radiation and conduction of heat occurs, and that heat cannot of itself pass from a body at a lower temperature to one at a higher: we are then justified in assuming τ to be absolute temperature, which thus obtains a perfectly precise mathematical definition, as the reciprocal of an integrating factor of dH , and we are brought back to Sir W. Thomson's absolute scale.

50. Connection between the two laws of thermodynamics. Attempts have been made to deduce the second law from the first, by the aid of mechanical principles or mechanical assumptions only, but in general these assumptions are no more obvious than the thermal axioms of § 38: thus Professors Rankine, Boltzmann, and Clausius have given demonstrations, the first on the hypotheses of molecular vortices¹ and circulating streams², the second on that of periodic motions³, and the third on that of quasi-periodic motions⁴.

Hr. Szily has given the following demonstration⁵. The S, I, W of § 31 are respectively the K, P, W of § 4; hence

$$S = \Sigma \cdot \frac{1}{2} \mu (\dot{x}^2 + \dot{y}^2 + \dot{z}^2),$$

¹ *Trans. R. S. E.* xx. (1851) 205.

² *Phil. Mag.* [4] x. (1855) 416.

³ See Mr. Burbury's simplified proof in *Phil. Mag.* [5] i. (1876) 61, or in Mr. Watson's *Kinetic Theory of Gases* (1876), 46.

⁴ *Pogg. Ann.* cxlii. (1871) 433.

⁵ *Műegyetemi Lapok*, i. (1876) 165, trans. *Phil. Mag.* [5] ii. (1876) 254.

$$\delta I + \delta W = \delta \chi = -\Sigma \cdot \mu (\ddot{x} \delta x + \ddot{y} \delta y + \ddot{z} \delta z),$$

$$\delta H = \delta S + \delta I + \delta W = \delta S - \Sigma \cdot \mu (\ddot{x} \delta x + \ddot{y} \delta y + \ddot{z} \delta z).$$

But, if τ denotes time, we have also

$$\delta S = \Sigma \cdot \mu (\dot{x} \delta \dot{x} + \dot{y} \delta \dot{y} + \dot{z} \delta \dot{z}),$$

$$d(\dot{x} \delta x) = \dot{x} d \delta x + d \dot{x} \delta x = \dot{x} d \delta x + \ddot{x} d\tau \delta x,$$

and similar equations in y and z : hence

$$\begin{aligned} \delta \int_0^\tau 2 S d\tau &= \delta \int \Sigma \cdot \mu (\dot{x} dx + \dot{y} dy + \dot{z} dz) \\ &= \int \Sigma \cdot \mu (\dot{x} d \delta x + \dot{y} d \delta y + \dot{z} d \delta z + \delta \dot{x} dx + \delta \dot{y} dy + \delta \dot{z} dz) \\ &= \int \Sigma \cdot \mu \{ d(\dot{x} \delta x + \dot{y} \delta y + \dot{z} \delta z) - (\ddot{x} \delta x + \ddot{y} \delta y + \ddot{z} \delta z) d\tau \\ &\quad + (\dot{x} \delta \dot{x} + \dot{y} \delta \dot{y} + \dot{z} \delta \dot{z}) d\tau \} \\ &= \left[\Sigma \cdot \mu (\dot{x} \delta x + \dot{y} \delta y + \dot{z} \delta z) \right]_0^\tau + \int_0^\tau \delta H d\tau. \end{aligned} \quad (16)$$

If the initial and final values of $\Sigma \cdot \mu (\dot{x} \delta x + \dot{y} \delta y + \dot{z} \delta z)$ are equal, and if $\overline{\delta H}$, \overline{S} represent the mean energy communicated to the system per unit of time and the mean kinetic energy during the interval τ respectively, then

$$\tau \overline{\delta H} = \delta \cdot 2 \tau \overline{S}. \quad (17)$$

Now we cannot assume that the thermal state of any body or system is ever absolutely the same at two successive instants; for it is composed of numberless molecules which are in continual vibratory or progressive motion, and only those molecules are in the same positions in successive instants whose velocity happens for the time to be zero. There will therefore be continually varying rarefactions and condensations, and, as the chance of these rarefactions and condensations exactly compensating each other is infinitely small, it follows that the volume of the body must be subject to a continual variation which is periodic and of very small magnitude. When therefore we speak of the specific volume of a body we mean really the mean volume occupied by unit-mass during the period of this *pulsation*, as Hr. Szily calls it, and when the specific volume remains constant, the period of the pulsation must be constant too.

During these changes of volume work will also be done, which is zero in a complete pulsation; there are similarly variations of the kinetic energy S , the potential energy I , the intrinsic-energy E , and it is the mean values of these functions during the pulsation that we take to characterize the thermal state of the body. Further these changes occur adiabatically, for

$$\begin{aligned} dH &= dS + (dI + dW) = \Sigma . \mu \{ \dot{x} dx + \dots - \ddot{x} dx - \dots \} , \\ &= \Sigma . \mu \{ \dot{x} \ddot{x} + \dots - \ddot{x} \dot{x} - \dots \} d\tau = 0. \end{aligned}$$

Hence if we take τ the period of the pulsation, and write d instead of δ , we have on integration through any closed cycle

$$\int_0^\tau dH d\tau = 0,$$

since τ and \bar{S} at the close resume their initial values.

Or we may write (17) as

$$\frac{\overline{dH}}{\bar{S}} = 2d . \log \tau \bar{S}, \quad (18)$$

and therefore on integrating over a complete cycle we get

$$\int \frac{\overline{dH}}{\bar{S}} = 0.$$

This is the second law of thermodynamics, since \bar{S} is proportional to the absolute temperature (see § 64).

The values of $\Sigma . \mu (\dot{x} \delta x + \dot{y} \delta y + \dot{z} \delta z)$ have been taken equal at the beginning and end of the interval τ ; for

$$\left[\Sigma . \mu (\dot{x} \delta x + \dot{y} \delta y + \dot{z} \delta z) \right]_0^\tau = \delta . 2 \tau \bar{S} - \tau \overline{\delta H} = 0,$$

since, when no energy is added to a system, the period of the pulsation is constant and the mean kinetic energy undergoes no change.

If however what we say in § 38 is true, then no proof of the second law can be deduced directly from known dynamical principles: and any such deduction, wherein probability has not been taken into account, must be imperfect, however satisfactory it may appear.

NON-REVERSIBLE PROCESSES.

51. Non-reversible cycles. In the cycles hitherto considered we have supposed equation (2) § 31 to hold, that is, the following conditions to be satisfied: (i) the body is never in presence of others whose temperature is not infinitely near its own, (ii) the external pressure never differs more than infinitesimally from the stress exerted by the body, (iii) the changes of density occur with exceeding slowness, (iv) no heat is spent in overcoming friction or transformed into magnetic or electric energy: in all such cases the cycles are reversible.

In other cases we cannot perform the process in exactly the reversed order, and these are called *non-reversible* cycles. In their case the equation

$$\int dH = W$$

must hold, as it expresses the Conservation of Energy: but we have always

$$\int \frac{dH}{T} < 0; \quad (19)$$

for we have shewn in § 46 that the transformations of any cycle may be reduced to the transformation of heat \mathfrak{h} from the lower temperature T_0 to the higher T , and that \mathfrak{h} cannot therefore be positive, but we cannot in this case reverse the cycle and shew that \mathfrak{h} cannot be negative. Thus for non-reversible cycles \mathfrak{h} is negative, or the sum of the transformations is a negative transformation: whence, calling a transformation *uncompensated* which occurs without any accompanying change, we may say:—*uncompensated transformations can only be negative, that is, of work into heat and of heat from higher to lower temperatures.*

M. Verdet¹ has shewn in detail that neglect of any of the above conditions entails a negative value for the integral $\int \frac{dH}{T}$: the student should have no difficulty in shewing this for himself.

In the case of a non-reversible process that does not form a closed cycle, as ABC in Fig. 25, we may, following M. Clausius², complete the cycle as therein done by the adiabatic

¹ *Théorie mécanique de la Chaleur* (1868), i. 188.

² *Pogg. Ann.* xcvi. (1856) 452, trans. *Phil. Mag.* [4] xii. (1856) 248.

through C and the isothermal through A : then the integral over the whole cycle $ABCD A$

$$\int \frac{dH}{T} \equiv \int_A^C \frac{dH}{T} + \int_C^A \frac{dH}{T} < 0;$$

but $\int_C^A \frac{dH}{T}$ is by § 47 equal to $\phi_A - \phi_C$, whence

$$\int_A^C \frac{dH}{T} < \phi_C - \phi_A. \quad (20)$$

CHAPTER V.

Fundamental Equations.

52. Application of the First Law. Recalling the equations of §§ 15, 31, we have

$$dE + p \, dv = dH = k \, dt + l \, dv,$$

or
$$dE = k \, dt + (l - p) \, dv. \quad (1)$$

But dE is an exact differential: hence

$$\frac{\partial}{\partial v} k = \frac{\partial}{\partial t} (l - p),$$

or
$$\frac{\partial l}{\partial t} - \frac{\partial k}{\partial v} = \frac{\partial p}{\partial t}. \quad (2)$$

This equation was first given by Professor Clausius¹, but by a somewhat tedious method; the above is Sir W. Thomson's very precise demonstration². But for this relation we should have had no reason for thinking that l and k are not entirely independent of each other.

By similar methods we may get the corresponding equations

$$\frac{\partial K}{\partial p} - \frac{\partial L}{\partial t} = \frac{\partial v}{\partial t}, \quad (3)$$

$$\frac{\partial v}{\partial p} - \frac{\partial v}{\partial v} = 1, \quad (4)$$

the last being already given in § 49.

53. Application of the Second Law. This is expressed by taking $\frac{dH}{t}$ an exact differential: hence the function

$$\frac{k}{t} \, dt + \frac{l}{t} \, dv$$

¹ *Pogg. Ann.* lxxix. (1850) 384, trans. *Phil. Mag.* [4] ii. (1851) 11.

² *Trans. R. S. E.* xx. (1851) 270, or *Phil. Mag.* [4] iv. (1852) 19.

is an exact differential, so that

$$\frac{\partial}{\partial v} \cdot \frac{k}{t} = \frac{\partial}{\partial t} \cdot \frac{l}{t}, \quad (5)$$

which becomes on simplification

$$\frac{\partial l}{\partial t} - \frac{\partial k}{\partial v} = \frac{l}{t},$$

whence by (2)

$$\frac{\partial p}{\partial t} = \frac{\partial l}{\partial t} + \frac{\partial k}{\partial v} = \frac{l}{t}. \quad (6)$$

This is the result found directly in § 48 from Carnot's principle. We also obtain from (5) and (6)

$$\frac{\partial k}{\partial v} = t \frac{\partial}{\partial t} \cdot \frac{l}{t} = t \frac{\partial^2 p}{\partial t^2}. \quad (7)$$

By using the other expressions for dH in a similar manner we find

$$\frac{\partial v}{\partial t} = \frac{\partial K}{\partial p} - \frac{\partial L}{\partial t} = -\frac{L}{t}, \quad (8)$$

$$\frac{\partial K}{\partial p} = -t \frac{\partial^2 v}{\partial t^2}, \quad (9)$$

and

$$1 = \frac{\partial v}{\partial p} - \frac{\partial p}{\partial v} = \frac{1}{t} \left(v \frac{\partial t}{\partial p} - p \frac{\partial t}{\partial v} \right). \quad (10)$$

54. Values of the Specific Heats. If k , \mathfrak{k} represent functions of t , the probable values of which will be found in § 65, equations (7) and (9) give respectively

$$k = \mathfrak{k} + t \int \frac{\partial^2 p}{\partial t^2} dv, \quad (11)$$

$$K = \mathfrak{K} - t \int \frac{\partial^2 v}{\partial t^2} dp. \quad (12)$$

the integrals being *indefinite*—which is obvious, since the specific heat of a body can depend only on its actual state. If the integrals are taken *definitely*, then \mathfrak{k} , \mathfrak{K} are not functions of t only but are the values of k , K at the lower limit. As t is to be taken constant in evaluating these integrals, it is convenient to introduce two quantities w , w' to represent respectively the indefinite integrals $\int p dv$, $\int v dp$ wherein t is constant, these quantities being obviously connected by the relation

$$pv = w + w' + \text{const.}$$

The above equations then become, with the notation of § 15,

$$k = \mathfrak{k} + t \frac{\partial^2 w}{\partial t^2}, \quad (13)$$

$$K = \mathfrak{K} - t \left(\frac{\partial^2 w'}{\partial t^2} \right), \quad (14)$$

From (6) § 16 and (6) we have

$$\begin{aligned} K - k &= t \frac{\partial v}{\partial t} = t \frac{\partial p}{\partial t} \frac{\partial v}{\partial t} \\ &= -t \frac{\left(\frac{\partial p}{\partial t} \right)^2}{\frac{\partial p}{\partial v}} \quad \text{or} \quad -t \frac{\left(\frac{\partial v}{\partial t} \right)^2}{\frac{\partial v}{\partial p}}. \end{aligned} \quad (15)$$

These equations may also be got from (8) § 16 and (8), or from (9) § 16 and (10). Hence we may remark that K is always greater than k ; for $\frac{\partial p}{\partial v}$ is always negative and the sign of $\frac{\partial p}{\partial t}$ is without influence.

The characteristic equations corresponding to the bodies for which this difference $K - k$ is always a constant quantity R are easily found from the partial differential equation: it gives two complete primitives,

$$\begin{aligned} (p - a)(v - b) &= Rt, \\ p - b &= 2at^{\frac{1}{2}} - \frac{a^2}{R}v, \end{aligned}$$

wherein a and b are arbitrary constants. A particular case of the former is the equation to a perfect gas.

When this difference is a function of t we find one complete primitive only,

$$p - b = a\mathfrak{U} - a^2v,$$

where \mathfrak{U} is a function of t related to the given function, a and b being arbitrary constants.

55. Difference of the Elasticities. From § 17 we have

$$\epsilon_t = -v \frac{\partial p}{\partial v}, \quad \epsilon_H = -\kappa v \frac{\partial p}{\partial v};$$

hence

$$\epsilon_H - \epsilon_t = -\frac{K - k}{k} v \frac{\partial p}{\partial v} = \frac{vt}{k} \left(\frac{\partial p}{\partial t} \right)^2, \quad (16)$$

and similarly

$$\frac{1}{\epsilon_t} - \frac{1}{\epsilon_H} = \frac{t}{Kv} \left(\frac{\partial v}{\partial t} \right)^2. \quad (17)$$

56. General Equation. This may now by (13) be written

$$dH = k dt + t \frac{\partial^2 w}{\partial t^2} dt + t \frac{\partial p}{\partial t} dv \quad (18)$$

$$= k dt + t d \cdot \frac{\partial w}{\partial t}. \quad (19)$$

And by (14) we have similarly, when t and p are the variables,

$$dH = k dt - t d \cdot \left(\frac{\partial w'}{\partial t} \right)_p. \quad (20)$$

57. Determination of the Intrinsic Energy. By (18) we have,

$$\begin{aligned} dE = dH - p dv &= k dt + t \frac{\partial^2 w}{\partial t^2} dt + \left(t \frac{\partial p}{\partial t} - p \right) dv \\ &= k dt + d \cdot \left(t \frac{\partial w}{\partial t} - w \right), \end{aligned} \quad (21)$$

the complete integral of which is

$$E - E_0 = \int_{t_0}^t k dt + \left(t \frac{\partial w}{\partial t} - w \right) - \left(t_0 \frac{\partial w_0}{\partial t_0} - w_0 \right), \quad (22)$$

the suffixes denoting the values corresponding to the initial condition.

If the intrinsic energy is required in terms of p and t —the use of which variables is limited, as we have already noticed—equation (20) gives

$$dE = k dt - d \cdot \left\{ t \left(\frac{\partial w'}{\partial t} \right)_p - w' + pv \right\},$$

whence,

$$\begin{aligned} E - E_0 &= \int_{t_0}^t k dt - (pv - p_0 v_0) - \left\{ t \left(\frac{\partial w'}{\partial t} \right)_p - w' \right\} \\ &\quad + \left\{ t_0 \left(\frac{\partial w'_0}{\partial t_0} \right)_p - w'_0 \right\}. \end{aligned} \quad (23)$$

We can determine the intrinsic energy directly from the equation

$$dE = k dt + \left(t \frac{\partial p}{\partial t} - p \right) dv, \quad (24)$$

the integral of which is

$$E - E_0 = \int_{t_0}^t k_{v_0} dt + \int_{v_0}^v \left(t \frac{\partial p}{\partial t} - p \right) dv; \quad (25)$$

since (v. Professor Price's *Int. Calc.* § 372) if

$$du = f(x, y) dx + \phi(x, y) dy$$

be an exact differential, its integral is

$$\begin{aligned} u - u_0 &= \int_{x_0}^x f(x, y) dx + \int_{y_0}^y \phi(x_0, y) dy \\ &= \int_{y_0}^y \phi(x, y) dy + \int_{x_0}^x f(x, y_0) dx. \end{aligned} \quad (26)$$

Similarly, with p and t as the variables, the equation

$$dE = (K - p \frac{\partial v}{\partial t}) dt - (t \frac{\partial v}{\partial t} + p \frac{\partial v}{\partial p}) dp$$

gives the integral

$$E - E_0 = \int_{t_0}^t K_{p_0} dt - p_0(v - v_0)_{p_0} - \int_{p_0}^p (t \frac{\partial v}{\partial t} + p \frac{\partial v}{\partial p}) dp. \quad (27)$$

These equations were first given in a slightly different form by Sir W. Thomson¹, who thus shews that the variation of E may be determined without experiment if we know the equation connecting p , v , t and the thermal capacity for any particular constant density or pressure and all temperatures.

We have also

$$\frac{\partial E}{\partial v} = t \frac{\partial p}{\partial t} - p,$$

which gives on integration

$$p = t\mathfrak{V} + t \int \frac{1}{t^2} \frac{\partial E}{\partial v} dt,$$

where \mathfrak{V} represents a function of v , the integral being indefinite; if we take the integral definite, the equation becomes

$$\frac{p}{t} = \frac{p_0}{t_0} + \int_{t_0}^t \frac{1}{t^2} \frac{\partial E}{\partial v} dt.$$

Hence for the intrinsic energy to be a function of the temperature only we must have

$$p = t\mathfrak{V};$$

in this case the internal work must be independent of both density and pressure. These are therefore properties that belong to a perfect gas.

58. Professor Rankine's method. The equations we have obtained so far are derived entirely from the two laws of thermodynamics, and are perfectly independent of all hypotheses as to the molecular constitution and physical properties of

¹ *Trans. R. S. E.* xx. (1851) 479, or *Phil. Mag.* [4] ix. (1855) 527.

bodies; they contain such quantities only as are capable of direct measurement. For further development of the theory (indicated in §§ 26–29) certain hypotheses have been introduced; and though these take us out of the domain of pure thermodynamics into that of molecular dynamics, yet we shall briefly discuss the results so obtained, mindful however of their hypothetical nature.

Professor Rankine¹ assumes the whole of the first term of the right-hand expressions of equations (18) and (19) to represent the increment of the sensible heat in the body: this assumption is really double—(1) that the sensible heat in a body is independent of its density or the arrangement of its molecules; (2) that the expression for the internal work during any change contains no term depending on the temperature only. On these suppositions equation (18) may thus be analysed:—

(α) the variation κdt or dS of the sensible heat of unit-mass;

(β) the work $t \frac{\partial^2 w}{\partial t^2} dt$ done against molecular action in the small increase dt of temperature;

(γ) the work $t \frac{\partial p}{\partial t} dv$ done against molecular action and also against external resistance in the small increase dv of volume, so that the work done on this account against molecular action only is $(t \frac{\partial p}{\partial t} - p) dv$.

The total internal work done is therefore

$$dI = t \frac{\partial^2 w}{\partial t^2} dt + (t \frac{\partial p}{\partial t} - p) dv = d \cdot (t \frac{\partial w}{\partial t} - w),$$

whence its absolute value for any state of a body is

$$I = t \frac{\partial w}{\partial t} - w + \mathfrak{I}, \quad (28)$$

as we might have inferred from (22), \mathfrak{I} being the constant of § 29

¹ *A Manual of the Steam Engine, &c.*, 4th ed. (1869), 312.

Professor Rankine defines also another function ϕ such that

$$dH = t d\phi; \quad (29)$$

we therefore have

$$d\phi = \frac{\kappa}{t} dt + d \cdot \frac{\partial w}{\partial t},$$

and, on integration,

$$\phi - \phi_0 = \int_{t_0}^t \frac{\kappa}{t} dt + \frac{\partial w}{\partial t} - \frac{\partial w_0}{\partial t_0}, \quad (30)$$

where ϕ_0 is the value of the function in the initial state corresponding to p_0, v_0, t_0 . ϕ is called the *thermodynamic function* for the kind of work under consideration, and the quantity $\frac{\partial w}{\partial t}$ is called the *heat-potential* or *melamorphic function* of the substance for the work in question.

The further assumption that κ is a constant quantity for each substance whatever its state (see § 65) leads to the equation

$$\phi - \phi_0 = \kappa \log_e t + \frac{\partial w}{\partial t} - \left(\kappa \log_e t_0 + \frac{\partial w_0}{\partial t_0} \right). \quad (31)$$

59. Professor Clausius' method. The assumption in this method is that 'the mechanical work which can be done by heat during any change of the arrangement of a body is proportional to the absolute temperature at which this change occurs¹.' The justification of this assumption is referred to 'internal probability,' which is however scarcely obvious: we must rather judge of it by its results, and it seems to be true with perfect gases and for thermo-electricity². A new magnitude *disgregation* is introduced to express the degree in which the molecules of a body are separated from each other. Now the action of heat is to alter the disgregation, and it is by this action that work is done whether internal or external: hence, according to the assumed law, if in any reversible change a total amount of work $dI + dW$ is done, the disgregation Z must so be measured that

$$t dZ = dI + dW, \quad (32)$$

¹ Pogg. Ann. cxvi. (1862) 82, trans. Phil. Mag. [4] xxiv. (1862) 88.

² Pogg. Ann. xc. (1853) 513.

and the general equation becomes, as in (5), § 31,

$$dH = d\dot{S} + t dZ. \quad (33)$$

Now dZ depends only on the arrangement of the molecules in given states, and is therefore an exact differential; $\frac{dH}{t}$ is also an exact differential, and therefore $\frac{dS}{t}$ must be so too, or S is a function of t only. This is what we have termed the first part of Professor Rankine's assumption.

If now we make the second part of Professor Rankine's assumption, we get

$$Z - Z_0 = \frac{\partial w}{\partial t} - \frac{\partial w_0}{\partial t_0}. \quad (34)$$

Professor Clausius does not however admit this generally, and therefore

$$Z - Z_0 = \int_{t_0}^t \mathfrak{U} dt + \frac{\partial w}{\partial t} - \frac{\partial w_0}{\partial t_0}. \quad (35)$$

Z_0 being the disgregation in the initial state, and \mathfrak{U} a function of t .

Hence Hr. Clausius arrives at an extension of his theorem of the equivalence of transformations. As an increase of disgregation is the conversion of heat into work, it is a positive transformation, and its equivalence-value is dZ , since this is by

definition $\frac{dI + dW}{t}$: now dH is the heat received by the body,

or we may say $-dH$ is the heat given up by the body to external objects, and dS is the heat that goes to increase the temperature; hence $dS - dH$ represents the heat converted into work, and its equivalence-value is $\frac{dS - dH}{t}$: also equation (28)

gives for any reversible process, which is not necessarily a cycle, the relation

$$\int \frac{dS - dH}{t} + \int dZ = 0:$$

therefore the algebraic sum of all the transformations in any reversible process is zero.

Omitting the condition of reversibility, and remarking that

no positive transformation can ever occur, as before shewn, without an accompanying negative one whose equivalence-value is at least as great, while a negative transformation can occur with a smaller positive one or even entirely uncompensated, we see that the change of disgregation can never be greater than that which corresponds to the work done, though it may be less, or

$$dz \leq \frac{dI + dW}{t} :$$

hence the general equation gives

$$\int \frac{dS - dH}{t} + \int dz \leq 0, \quad (36)$$

or the theorem takes its most general form:—the algebraic sum of all the transformations occurring during any change of condition whatever can only be negative, or, in the limiting case of reversibility, zero.

The integral $\int \frac{dS}{t}$ is called by Hr. Clausius the *transformation-value* of the heat actually present in a body when calculated from a given initial condition: the important integral $\int \frac{dH}{t}$, which we have before represented by $\int d\phi$ under the name of thermodynamic function, is called the *transformational-content* of the body, or its *entropy*¹. We shall adopt this last name, the term thermodynamic function not being sufficiently characteristic.

Hr. Clausius suggests² also the following nomenclature: *W* the external *ergon*; *I* the internal *ergon* or *ergonal-content* of the body; *S* the *thermal-content* of the body: thus the intrinsic energy *E* is the sum of the thermal and ergonal contents. Latent heats of expansion, fusion, evaporation, &c. are all varieties of *ergonized heat*, and are generally both internal and external.

¹ Pogg. Ann. cxxv. (1865) 390.

² Abhandlungen über die mechanische Wärmetheorie. Appendix to 6th Memoir.

80. Entropy. The entropy of a body is its property, expressed as a measurable quantity, which remains constant when heat is neither gained nor lost by the body, and which increases or diminishes according as heat enters or leaves it: for

$$d\phi = \frac{dH}{t}.$$

The isentropics and adiabatics of a body are therefore coincident, as stated in § 32, and their equations are $\phi = \text{const.}$

Just as we cannot determine the absolute value of the intrinsic energy of a body, since we cannot entirely deprive it of heat, so we cannot find the absolute value of its entropy: it is convenient therefore to reckon entropy from a definite state within the range of experiment. If then this state corresponds to p_0, v_0, t_0 , and it is the limit from which w is measured, then equation (31) gives the entropy

$$\phi' = k \log_e \frac{t}{t_0} + \frac{\partial w}{\partial t} - \frac{\partial w_0}{\partial t_0}. \quad (37)$$

As thus defined it is a relative quantity and may be negative: the absolute entropy of a body however is always positive.

The best method of determining the entropy of a body—by which is meant the entropy of unit-mass—is by performing two operations: (1) altering its state without addition or removal of heat till the temperature becomes t_0 , the entropy remaining unchanged during this process; (2) bringing its pressure to p_0 , the temperature being kept constantly t_0 : if h is the heat emitted during the latter process, absorption being reckoned negative, the entropy is lowered during this process by $\frac{h}{t_0}$, and this quantity is the relative entropy of the body in its original condition. The entropy of mass m is therefore $m \frac{h}{t_0}$; or, if in the above operation heat H is emitted by a mass m of the body, the entropy of unit-mass is $\frac{H}{mt_0}$.

If a body loses heat H at the constant temperature T its entropy is lessened by $\frac{H}{T}$, and if another body at constant

temperature t gains this heat, its entropy is increased by $\frac{H}{t}$: hence when heat H is transferred from a body at constant temperature T to another at constant temperature t , there is an increase in the entropy of the system equal to

$$\frac{H}{t} - \frac{H}{T} = \frac{T-t}{Tt} H.$$

Now the natural tendency of heat is to pass from hotter to colder bodies: hence Professor Clausius' theorem that *the entropy of a system tends to a maximum*¹.

61. General determination of intrinsic energy and entropy. Hr. Kirchhoff², wishing to obtain more general expressions, took as variables the absolute temperature t and an undefined magnitude x which may be the density, or pressure, or refractive index, &c.; Hr. Clausius³, by taking any two magnitudes x and y as variables, has introduced the utmost generality, and this method we will exhibit.

In the most general case we have

$$t d\phi = dH = dE + dW;$$

hence, employing no brackets as there is no ambiguity,

$$\frac{\partial E}{\partial x} = \frac{\partial H}{\partial x} - \frac{\partial W}{\partial x}, \quad \frac{\partial E}{\partial y} = \frac{\partial H}{\partial y} - \frac{\partial W}{\partial y}, \quad (38)$$

and therefore, as dE is an exact differential,

$$\begin{aligned} \frac{\partial}{\partial y} \left(\frac{\partial H}{\partial x} - \frac{\partial W}{\partial x} \right) &= \frac{\partial}{\partial x} \left(\frac{\partial H}{\partial y} - \frac{\partial W}{\partial y} \right), \\ \text{or} \quad \frac{\partial}{\partial y} \cdot \frac{\partial H}{\partial x} - \frac{\partial}{\partial x} \cdot \frac{\partial H}{\partial y} &= \frac{\partial}{\partial y} \cdot \frac{\partial W}{\partial x} - \frac{\partial}{\partial x} \cdot \frac{\partial W}{\partial y} \quad (39) \\ &= \mathfrak{E}_{xy} \end{aligned}$$

if we write \mathfrak{E}_{xy} for this function of W which we call *the ergonal difference corresponding to xy* . As further $\frac{dH}{t}$ is an exact differential, we have

$$\frac{\partial}{\partial y} \left(\frac{1}{t} \frac{\partial H}{\partial x} \right) = \frac{\partial}{\partial x} \left(\frac{1}{t} \frac{\partial H}{\partial y} \right),$$

¹ Pogg. Ann. cxxv. (1865) 400.

² Pogg. Ann. ciii. (1858) 177.

³ Pogg. Ann. cxxv. (1865) 359, and Schlämilch's *Zeitschrift für Math. und Phys.* xi. (1866) 31, trans. *Phil. Mag.* [4] xxxii. (1866) 1.

or
$$\frac{\partial}{\partial y} \cdot \frac{\partial H}{\partial x} - \frac{\partial}{\partial x} \cdot \frac{\partial H}{\partial y} = \frac{1}{t} \left(\frac{\partial H}{\partial x} \frac{\partial t}{\partial y} - \frac{\partial H}{\partial y} \frac{\partial t}{\partial x} \right),$$

whence, by (39),

$$\begin{vmatrix} \frac{\partial H}{\partial x}, & \frac{\partial H}{\partial y} \\ \frac{\partial t}{\partial x}, & \frac{\partial t}{\partial y} \end{vmatrix} = t \mathfrak{E}_{xy}. \quad (40)$$

On writing in (40) $t \frac{\partial \phi}{\partial x}$, $t \frac{\partial \phi}{\partial y}$ for $\frac{\partial H}{\partial x}$, $\frac{\partial H}{\partial y}$, we get

$$\begin{vmatrix} \frac{\partial \phi}{\partial x}, & \frac{\partial \phi}{\partial y} \\ \frac{\partial t}{\partial x}, & \frac{\partial t}{\partial y} \end{vmatrix} = \mathfrak{E}_{xy}; \quad (41)$$

also, since

$$\frac{\partial \phi}{\partial x} = \frac{1}{t} \frac{\partial E}{\partial x} + \frac{1}{t} \frac{\partial W}{\partial x}, \quad \frac{\partial \phi}{\partial y} = \frac{1}{t} \frac{\partial E}{\partial y} + \frac{1}{t} \frac{\partial W}{\partial y}, \quad (42)$$

and $d\phi$ is an exact differential, we have

$$\frac{\partial}{\partial y} \left(\frac{1}{t} \frac{\partial E}{\partial x} + \frac{1}{t} \frac{\partial W}{\partial x} \right) = \frac{\partial}{\partial x} \left(\frac{1}{t} \frac{\partial E}{\partial y} + \frac{1}{t} \frac{\partial W}{\partial y} \right),$$

whence
$$\begin{vmatrix} \frac{\partial E}{\partial x}, & \frac{\partial E}{\partial y} \\ \frac{\partial t}{\partial x}, & \frac{\partial t}{\partial y} \end{vmatrix} = t^2 \left(\frac{\partial}{\partial y} \cdot \frac{1}{t} \frac{\partial W}{\partial x} - \frac{\partial}{\partial x} \cdot \frac{1}{t} \frac{\partial W}{\partial y} \right); \quad (43)$$

$$= \mathfrak{E}'_{xy},$$

if we write \mathfrak{E}'_{xy} for this function of W , the relation between \mathfrak{E}_{xy} and \mathfrak{E}'_{xy} being obviously

$$\mathfrak{E}'_{xy} = t \mathfrak{E}_{xy} - \begin{vmatrix} \frac{\partial \omega}{\partial x}, & \frac{\partial \omega}{\partial y} \\ \frac{\partial t}{\partial x}, & \frac{\partial t}{\partial y} \end{vmatrix} \quad (44)$$

If we had taken ξ, η as variables instead of x, y , we should have found similar expressions, and since

$$\frac{\partial W}{\partial \xi} = \frac{\partial W}{\partial x} \frac{\partial x}{\partial \xi} + \frac{\partial W}{\partial y} \frac{\partial y}{\partial \xi}, \quad \frac{\partial W}{\partial \eta} = \frac{\partial W}{\partial x} \frac{\partial x}{\partial \eta} + \frac{\partial W}{\partial y} \frac{\partial y}{\partial \eta},$$

we easily find

$$\frac{\mathfrak{E}_{\xi\eta}}{\mathfrak{E}_{xy}} = \frac{\mathfrak{E}'_{\xi\eta}}{\mathfrak{E}'_{xy}} = \begin{vmatrix} \frac{\partial x}{\partial \xi}, & \frac{\partial x}{\partial \eta} \\ \frac{\partial y}{\partial \xi}, & \frac{\partial y}{\partial \eta} \end{vmatrix}. \quad (45)$$

Hence, replacing only one of the variables y by η , we have $x = \xi$, $\frac{\partial x}{\partial \xi} = 1$, $\frac{\partial x}{\partial \eta} = 0$, and by (45)

$$\mathfrak{E}_{x\eta} = \frac{\partial y}{\partial \eta} \mathfrak{E}_{xy}, \quad \mathfrak{E}'_{x\eta} = \frac{\partial y}{\partial \eta} \mathfrak{E}'_{xy}. \quad (46)$$

The equations (41) and (43) are the most general for the entropy and intrinsic energy: they reduce to Hr. Kirchhoff's if t be put for y ; for then $\frac{\partial t}{\partial y} = 1$, $\frac{\partial t}{\partial x} = 0$, and

$$\frac{\partial \phi}{\partial x} = \mathfrak{E}_{xt}, \quad \frac{\partial E}{\partial x} = \mathfrak{E}'_{xt}, \quad (47)$$

whence

$$\phi = \mathfrak{T} + \int \mathfrak{E}_{xt} dx, \quad E = \mathfrak{T}' + \int \mathfrak{E}'_{xt} dx, \quad (48)$$

\mathfrak{T} , \mathfrak{T}' being functions of t ; or we have

$$d\phi = \frac{1}{t} \frac{\partial H}{\partial t} dt + \mathfrak{E}_{xt} dx, \quad dE = \left(\frac{\partial H}{\partial t} - \frac{\partial W}{\partial t} \right) dt + \mathfrak{E}'_{xt} dx,$$

whence, by (26),

$$\left. \begin{aligned} \phi - \phi_0 &= \int_{t_0}^t \frac{1}{t} \left[\frac{\partial H}{\partial t} \right]_{x_0} dt + \int_{x_0}^x \mathfrak{E}_{xt} dx, \\ E - E_0 &= \int_{t_0}^t \left[\frac{\partial H}{\partial t} - \frac{\partial W}{\partial t} \right]_{x_0} dt + \int_{x_0}^x \mathfrak{E}'_{xt} dx. \end{aligned} \right\} \quad (49)$$

In the particular case where $dW = p dv$, we have

$$\mathfrak{E}_{xy} = \begin{vmatrix} \frac{\partial v}{\partial x}, & \frac{\partial v}{\partial y} \\ \frac{\partial p}{\partial x}, & \frac{\partial p}{\partial y} \end{vmatrix}, \quad \mathfrak{E}'_{xy} = \begin{vmatrix} \frac{\partial v}{\partial x}, & \frac{\partial v}{\partial y} \\ \frac{\partial \pi}{\partial x}, & \frac{\partial \pi}{\partial y} \end{vmatrix}, \quad (50)$$

if π is written for $\frac{p}{t}$: and the latter equation of (49) then gives (25) or (27) according as v or p is put for x .

62. Relations between partial differential coefficients. From the foregoing we may suppose ϕ and E known as well as

p, v, t ; hence we may take any two of these five quantities as variables and express the other three in terms of them: we can then find the partial differential coefficient of any one with regard to any other while a third remains constant. We have subjoined a table of the values of all such coefficients in terms of the specific heats and the simpler differential coefficients: the relations between them may then be deduced by inspection.

A single example will shew how the table has been constructed: thus, to find $(\frac{\partial E}{\partial \phi})_p$, we have

$$dE = t d\phi - p dv = \{t - p(\frac{\partial v}{\partial \phi})_p\} d\phi - p(\frac{\partial v}{\partial p})_p dp,$$

whence
$$(\frac{\partial E}{\partial \phi})_p = t - p(\frac{\partial v}{\partial \phi})_p;$$

but, since
$$d\phi = \frac{v}{t} dv + \frac{p}{t} dp,$$

we have
$$(\frac{\partial \phi}{\partial v})_p = \frac{v}{t} = \frac{K}{t} \frac{\partial t}{\partial v}, \text{ or } (\frac{\partial v}{\partial \phi})_p = \frac{t}{K} \frac{\partial v}{\partial t};$$

therefore
$$(\frac{\partial E}{\partial \phi})_p = \frac{t}{K} (K - p \frac{\partial v}{\partial t}).$$

We thus find by inspection

$$(\frac{\partial \phi}{\partial v})_p = (\frac{\partial p}{\partial t})_p, \quad (\frac{\partial \phi}{\partial p})_v = -(\frac{\partial v}{\partial t})_p,$$

$$\begin{vmatrix} \frac{\partial t}{\partial p} & \frac{\partial t}{\partial v} \\ \frac{\partial \phi}{\partial p} & \frac{\partial \phi}{\partial v} \end{vmatrix}_{pv} = 1 = \begin{vmatrix} \frac{\partial p}{\partial t} & \frac{\partial p}{\partial \phi} \\ \frac{\partial v}{\partial t} & \frac{\partial v}{\partial \phi} \end{vmatrix}_{t\phi},$$

&c., which relations might indeed be found by geometry: the last of them by (41) and (50) may be expressed as

$$\mathbb{E}_{vp} = 1 = \mathbb{E}_{\phi t}.$$

63. Application to perfect gases. The characteristic equation being

$$pv = R t,$$

we have

$$\frac{\partial p}{\partial t} = \frac{R}{v}, \quad \frac{\partial^2 p}{\partial t^2} = 0 \quad \text{and} \quad \frac{\partial v}{\partial t} = \frac{R}{p}, \quad \frac{\partial^2 v}{\partial t^2} = 0;$$

hence by (11) and (12)

$$k = \frac{R}{p}, \quad K = \frac{R}{p}, \quad (51)$$

or the specific heats are independent of the pressure or density.

By (15) we have

$$K - k = t \frac{\partial p}{\partial t} \frac{\partial v}{\partial t} = R, \quad (52)$$

or the difference between the specific heats is a constant quantity.

In this case

$$t \frac{\partial p}{\partial t} = p \text{ and therefore } t \frac{\partial w}{\partial t} = w;$$

hence by (22) the intrinsic energy is given by

$$E - E_0 = \int_{t_0}^t k \, dt, \quad (53)$$

or it is a function of the temperature only and entirely independent of the pressure and density.

On Professor Rankine's hypothesis, equation (28) shews that there is no heat spent in internal work, this being a constant quantity for all states of the gas,

$$I = 3. \quad (54)$$

Hr. Clausius' equation (35) gives us instead

$$Z - Z_0 = \int_{t_0}^t \mathfrak{T} \, dt + R \log_e \frac{v}{v_0}, \quad (55)$$

whence

$$t \, dZ = \mathfrak{T} \, t \, dt + R t \, d \cdot \log_e v = \mathfrak{T} \, t \, dt + p \, dv,$$

and therefore

$$I - I_0 = \int_{t_0}^t \mathfrak{T} \, t \, dt, \quad (56)$$

which vanishes only if \mathfrak{T} is zero, being in any case independent of the pressure and density. Thus no internal work is done in altering the volume of a perfect gas when its temperature remains constant; but this implies that its molecules are too far apart to act on each other, and therefore there cannot be any internal work at all however its state alters: hence for a perfect gas \mathfrak{T} must be zero. It must be zero therefore for all bodies that can be brought into the perfectly gaseous state, as it is a function of the temperature only and not of the density: to be as general as possible, however, Professor Rankine.

writes equation (31)—neglecting the constant—as

$$\phi = k \log_e t + t + \frac{\partial w}{\partial t}, \quad (57)$$

where t is 'a function of the temperature alone which is 0 for all temperatures at which the substance is capable of approximating indefinitely to the perfectly gaseous state, and is introduced into the formula solely to provide for the possible existence of substances which at some temperatures are incapable of approximating to the perfectly gaseous state¹.'

M. Regnault has shewn that K is constant for all rarefied permanent gases at all pressures and temperatures on the air-thermometer scale; this scale being very approximately the same as our absolute one, we may assume that for a perfect gas K , and therefore also k by (52), is constant. On this supposition (53) gives

$$E = kt + \mathfrak{J}, \quad (58)$$

where \mathfrak{J} is the constant of § 29 representing the molecular potential energy in the case of indefinite rarefaction, which is the whole intrinsic energy when the temperature is infinitely small.

Since K and k are constant, their ratio κ is so too, and therefore also by § 17 the ratio of the elasticity ϵ_H , which we may call the elasticity at constant entropy ϵ_ϕ , to the elasticity at constant temperature ϵ_t ; and we have

$$\epsilon_t = -v \frac{\partial p}{\partial v} = p, \quad \epsilon_\phi = \kappa \epsilon_t = \kappa p. \quad (59)$$

We may now find the equations to the thermal lines of a perfect gas. For the isothermals we have at once from the characteristic equation

$$pv = Rt = \text{const.}, \quad (60)$$

and thus the isothermals are equilateral hyperbolae.

Again, on the above assumption the isenergics are given by

$$pv = Rt = \frac{R}{k}(E - \mathfrak{J}) = \text{const.}, \quad (61)$$

¹ *Phil. Trans.* clx. (1870) 281.

and are therefore coincident with the isothermals. In this case therefore the points D , E of Fig. 25, § 47, coincide, as do the whole lines AD , AE .

The isentropics or adiabatics are also easily found ; for

$$\frac{l}{t} = \frac{\partial p}{\partial t} = \frac{R}{v} = \frac{K-k}{v},$$

and therefore

$$d\phi \equiv \frac{k}{t} dt + \frac{l}{t} dv \equiv k \left\{ \frac{dt}{t} + (\kappa-1) \frac{dv}{v} \right\} = 0,$$

which on integration gives

$$tv^{\kappa-1} = \text{const.}$$

Multiplying this first by $\frac{pv}{t}$ and secondly by $(\frac{t}{pv})^{\kappa-1}$, both which quantities are constant, we get

$$pv^{\kappa} = \text{const.}, \quad t^{\kappa} p^{1-\kappa} = \text{const.},$$

the former giving the adiabatics. These equations may be written

$$\frac{t}{t_0} = \left(\frac{v_0}{v}\right)^{\kappa-1}, \quad \frac{p}{p_0} = \left(\frac{v_0}{v}\right)^{\kappa}, \quad \frac{t}{t_0} = \left(\frac{p}{p_0}\right)^{\frac{\kappa-1}{\kappa}}, \quad (62)$$

the suffixes denoting initial values. These relations were found also by MM. Laplace¹ and Poisson² on the caloric theory of heat, as they too admitted that κ is constant.

We might have found the isenergics from the property of isentropics given in § 33; for

$$E_0 - \mathfrak{F} = \int_{v_0}^{\infty} p dv = p_0 v_0^{\kappa} \int_{v_0}^{\infty} \frac{dv}{v^{\kappa}} = \frac{p_0 v_0}{\kappa-1},$$

and p_0 , v_0 may be taken as the current coordinates corresponding to E_0 .

The work done by a perfect gas during any change at constant temperature is

$$W = \int_{v_0}^v p dv = Rt \int_{v_0}^v \frac{dv}{v} = Rt \log_e \frac{v}{v_0} = pv \log_e \frac{v}{v_0} \\ = p_0 v_0 \log_e \frac{v}{v_0} = p_0 v_0 \log_e \frac{p_0}{p}, \quad \left. \vphantom{\int_{v_0}^v} \right\} (63)$$

¹ *Mécanique céleste*, xii. 127.

² *Ann. de ch. et de ph.* [2] xxiii. (1823) 15, or *Traité de Mécanique*, 2^{de} éd. (1833), ii. 647.

and the work done along any isenergetic is given by the same expressions.

The work done along an isentropic or adiabatic is by (7), § 32,

$$W = E_0 - E = k(t_0 - t) = \frac{p_0 v_0}{\kappa - 1} \left(1 - \frac{t}{t_0}\right) \\ = k t_0 \left\{1 - \left(\frac{v_0}{v}\right)^{\kappa-1}\right\} = k t_0 \left\{1 - \left(\frac{p}{p_0}\right)^{\frac{\kappa-1}{\kappa}}\right\}. \quad (64)$$

If the curve were the more general one $p^m v^n = p_0^m v_0^n$, then the work done is

$$W = \int_{v_0}^v p dv = p_0 v_0^{\frac{n}{m}} \int_{v_0}^v \frac{dv}{v^{\frac{n}{m}}} = \frac{m}{n-m} p_0 v_0 \left\{1 - \left(\frac{v_0}{v}\right)^{\frac{n-m}{m}}\right\} \\ = \frac{m}{n-m} R(t_0 - t). \quad (65)$$

In this case the change of intrinsic energy being $k(t - t_0)$, we have to add heat equal to

$$\left(k + \frac{m}{m-n} R\right)(t - t_0) = \frac{mK - nk}{m-n}(t - t_0);$$

the quantity $\frac{mK - nk}{m-n}$ is called the specific heat of the gas relative to the change of state in question. For $m = n$ these formulae are indeterminate and we must proceed *ab initio* as above for the isothermals.

A numerical example or two will clear up all difficulties. We will suppose air to be a perfect gas—a very approximately true assumption if we take $-\frac{1}{0.003665}$ or -272.8°C. instead of -273.7°C. as absolute zero temperature. Further, the mass of 1 c.c. of air at 0°C. and under a barometric pressure of 76 c. in lat. 45° , that is, under a pressure of 1013226 dynes per square centimetre (see § 5), is 0.00129279 g., or the specific volume of this air is $\frac{1}{0.00129279} = 773.521$ c.c.: hence, measuring pressures in megadynes, we have

$$R = \frac{p_0 v_0}{t_0} = \frac{1.013226 \times 773.521}{272.8} = 2.8725.$$

The specific heat C is 0.2389 (Hr. Wiedemann's¹ value) or

$$K = 0.2389 \times 41.55 = 9.9263,$$

and

$$k = K - R = 7.0538, \quad \kappa = \frac{K}{k} = 1.4072.$$

¹ Pogg. Ann. clvii. (1876) 21.

Consider unit-mass of this air enclosed in a cylinder at 44°C. and under $1\frac{1}{2}$ atmospheres of pressure (*i.e.* $1\frac{1}{2}$ megadynes per sq. c.) so that

$$v_0 = \frac{2.8725 \times 316.8}{1.5} = 606.672 \text{ c.c. :}$$

let its pressure fall to 1 atmosphere—

(1) While it neither gains nor loses heat : here

$$\frac{v}{v_0} = \left(\frac{p_0}{p}\right)^{\frac{1}{\kappa}} = \left(\frac{3}{2}\right)^{\frac{1.4072}{2}} = \frac{4}{3}, \quad \therefore v = \frac{4}{3} \times 606.672 = 808.896 \text{ c.c.}$$

$$\frac{t}{t_0} = \frac{p}{p_0} \cdot \frac{v}{v_0} = \frac{2}{3} \cdot \frac{4}{3} = \frac{8}{9}, \quad \therefore t = \frac{8}{9} \times 316.8 = 281.6 = 8.8^{\circ}\text{C.}$$

$$W = k(t_0 - t) = 7.0538 \times \left(\frac{1}{9} \times 316.8\right) = 248.598 \text{ megalergs,}$$

and W measures the loss of intrinsic energy.

(2) While it is kept at constant temperature : here

$$\frac{v}{v_0} = \frac{p_0}{p} = \frac{3}{2}, \quad \therefore v = \frac{3}{2} \times 606.672 = 910.008 \text{ c.c.}$$

$$W = R t \log_e \frac{v}{v_0} = 2.8725 \times 316.8 \times (2.3026 \times \log 1.5) = 368.976 \text{ megalergs,}$$

and W measures the amount of heat that must be supplied.

(3) While it is kept at constant volume : here

$$\frac{t}{t_0} = \frac{p}{p_0} = \frac{2}{3}, \quad \therefore t = \frac{2}{3} \times 316.8 = 211.2^{\circ} \text{ or } -61.6^{\circ}\text{C.}$$

$$E - E_0 = k(t - t_0) = -7.0538 \times 105.6 = -745.795 \text{ megalergs,}$$

and this loss of intrinsic energy measures the heat that must be removed.

(4) Let it expand under constant pressure to the same volume as in (1),

i.e. to $\frac{4}{3}v_0$: here

$$\frac{t}{t_0} = \frac{v}{v_0} = \frac{4}{3}, \quad \therefore t = \frac{4}{3} \times 316.8 = 422.4^{\circ} \text{ or } 149.6^{\circ}\text{C.}$$

$$W = p_0(v - v_0) = 1.5 \times \left(\frac{1}{3} \times 606.672\right) = 303.336 \text{ megalergs.}$$

$$E - E_0 = k(t - t_0) = 7.0538 \times \left(\frac{1}{3} \times 316.8\right) = 745.795 \text{ megalergs,}$$

and the heat that must be supplied is

$$E - E_0 + W = 1049.131 \text{ megalergs.}$$

64. Sensible heat. We have presented in § 18 the arguments in favour of supposing sensible heat to be molecular kinetic energy, and therefore in all probability independent of the density, and we have seen in § 59 how Hr. Clausius' hypothesis leads to the same result—viz. that it is a function of

the temperature only. The question now arises whether all the heat contained in a body is at the temperature of the body, and Hr. Clausius concludes¹ that 'we must not ascribe one and the same temperature to the whole quantity of heat; we must rather conceive this whole quantity to be divided into an infinite number of elements, and to each element we must consider that temperature to correspond which the body on cooling would have at the moment when it parted with this element, or that which on being heated it would have at the moment when it received this element of heat.' For the transformation-value of the heat put into unit-mass to raise its temperature from that of its initial condition is $\int \frac{dS}{t}$, so that each increment of heat

spent in raising the temperature is a function of the temperature at which it is taken. And unless we accept this conclusion Hr. Clausius' fundamental axiom is contradicted in the following process which was suggested² by M. Hirn.

M. Hirn considered a theoretical machine consisting of two cylinders *A* and *B* equal in section and communicating with each other by the tube *O* which opens into their bases: they are provided with pistons which move without any friction, and the piston rods are indented and work into the teeth of the same wheel, so that one piston will always move up as much as the other moves down, the volume between them being therefore constant. The cylinders contain perfect gas, and, the pressure being therefore the same throughout, the pistons are in equilibrium in any position: hence no work will be done in any small motion of the pistons and therefore in any motion so long as it is slow enough. The whole apparatus is supposed impermeable by heat except the tube of communication which is kept at the constant temperature *S*. Consider now p_0 , v_0 , t_0 to

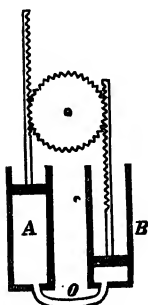


Fig. 26.

¹ *Pogg. Ann.* cxx. (1863) 449.

² *Théorie mécanique de la Chaleur*, 3^{ème} éd. (1875), i. 255.

characterise unit-mass of the gas initially when it is all collected in the cylinder A (the piston of B being in its lowest position), and suppose the total mass is M and the constant volume between the pistons V . The piston of A is then depressed and each successive portion of gas is heated to \mathfrak{S} as it passes through the tube O ; it therefore expands or tends to expand, and thus increases the pressure, causing in consequence an increase in temperature in every other part of the vessel. When all the gas is transferred to B , we shall, by reason of the extremely low conductivity of gases, have a series of layers at different temperatures, that of the lowest layer being \mathfrak{S} , and that of the highest much above \mathfrak{S} , and it thus appears that without the expenditure of work we have caused heat to pass from the tube O to gas at a higher temperature—which is contrary to our axiom.

We will calculate the mean temperature T in B . If t is the temperature at any moment of a layer of gas dm either in A or B , the pressure throughout the vessel being p and the specific volume of this particular layer v , then

$$\int v dm = V, \quad \int t dm = MT;$$

and, since the relation $pv = Rt$ always subsists,

$$p \int v dm = \int p v dm = R \int t dm,$$

or

$$pV = RMT;$$

but we have further

$$RM = \frac{p_0}{t_0} v_0 M = \frac{p_0}{t_0} V,$$

and therefore

$$\frac{p}{p_0} = \frac{T}{t_0}.$$

Now the temperature of the gas in A has become t by the alteration of the pressure without the communication of heat; hence by (62)

$$t = t_0 \left(\frac{p}{p_0} \right)^{\frac{\kappa-1}{\kappa}} = t_0 \left(\frac{T}{t_0} \right)^{\frac{\kappa-1}{\kappa}} = t_0^{\frac{1}{\kappa}} T^{\frac{\kappa-1}{\kappa}}$$

Again, as the mass dm of gas passes through the tube, its temperature is raised from t to \mathfrak{S} , and it slightly expands since it modifies the total pressure only infinitely little: hence it takes in heat at constant pressure and not at constant volume, and the heat thus taken in is, by § 15,

$$dm \int_t^{\mathfrak{S}} \frac{1}{K} dt = K (\mathfrak{S} - t) dm = K (\mathfrak{S} - t_0^{\frac{1}{\kappa}} T^{\frac{\kappa-1}{\kappa}}) dm:$$

this causes a variation dT in the mean temperature of the whole mass at constant volume, whence

$$Mk dT = K (\mathfrak{S} - t_0^{\frac{1}{\kappa}} T^{\frac{\kappa-1}{\kappa}}) dm,$$

integration of which from 0 to M (*i.e.* corresponding to the passage of all the gas into B) gives

$$\int_{t_0}^T \frac{dT}{\mathfrak{S} - t_0^{\frac{1}{\kappa}} T^{\frac{\kappa-1}{\kappa}}} = \kappa,$$

and the solution of this equation will give T , the final mean temperature.

If we put $t_0^{\frac{1}{\kappa}} T^{\frac{\kappa-1}{\kappa}} = \mathfrak{S}x$, so that $x_0 = \frac{t_0}{\mathfrak{S}}$, the equation becomes

$$\int_{x_0}^x \frac{x^{\frac{\kappa-1}{\kappa}}}{1-x} dx = (\kappa-1) x_0^{\frac{1}{\kappa-1}}.$$

Taking rarefied air to represent perfect gas we may assume $\kappa = 1.4072$, or $\frac{1}{\kappa-1} = 2.456$: then, if $x_0 = 0.5$ so that the value of the constant is 0.0742, an approximate calculation gives $x = 0.6306$, whence if t_0 be 0°C . or 272.8° (see § 63) and therefore $\mathfrak{S} = 545.6^\circ$ or 272.8°C ., we find $T = 607.6^\circ$ or 334.8°C , which is 62 degrees above the temperature of the tube.

If the heat in the gas were all at the temperature T , then the axiom could no longer hold; as without any expenditure of work a body would have been raised to a higher temperature than that of the source of heat: Hr. Clausius however points out that for any part of the gas in B to be raised above \mathfrak{S} heat must be given to some part of the gas in A at a temperature lower than \mathfrak{S} , and this is the compensation that renders the phenomenon possible. We shall shew in § 66 that no work is gained by the process.

65. Real specific heat. The coefficient $\frac{dS}{dt}$ or k is termed indifferently the *real specific heat*, the *capacity for heat*, or the *absolute thermal capacity* of a body, these names being intended to signify that it is independent of the density, *i.e.* of the molecular arrangement of the body. Now in one series of arrangements—those of the perfectly gaseous state—it is independent of the temperature also, and it is therefore probably constant in all arrangements. Professor Rankine considers it to be

constant only throughout each of the different states of aggregation, solid, liquid, or gaseous, in which a body may exist, and to differ in the different states¹; Hr. Clausius however points out² that molecular alterations are going on just as much, though in a less degree, in any one state as in the passage from one state to another, and that therefore it is rather arbitrary to assume for the smaller changes what is denied for the larger.

Hence we assume k to be constant for each substance, and, to determine it therefore, we ought to determine the specific heat at constant volume of the substance when in the state of a perfect gas, *i.e.* of highly superheated vapour. This operation is however doubly difficult: for the conversion into perfect gas of most substances requires temperatures not readily at our command, and the specific heat at constant volume of even an ordinary gas has as yet been only approximately determined (see § 74). MM. Dulong and Petit's law however, that *the specific heat of unit-mass of all bodies is inversely proportional to the atomic weight*, or *that the atomic heat of all bodies is the same*, comes to our aid: this law cannot indeed be true for the specific heats at constant pressure, as its discoverers imagined, by reason of the varying external and internal work; but Avogadro's law, that in equal volumes of all substances in the perfect state at the same pressure and temperature there is the same number of atoms, coupled with MM. Delaroche and Bérard's experimental conclusion that equal volumes of substances in the perfect state require equal amounts of heat for an equal rise in temperature, gives

$$nak = \text{const.} \quad \text{or} \quad ak = \text{const.},$$

where n is the number of atoms in a given volume and a the atomic weight: thus the specific heat in the above law is the real specific heat, as has been proved otherwise by M. Moutier³. To determine this constant we will take the case of the most perfect gas, hydrogen: now since the mass of 1 c.c. at 0°C. under a pressure of 76 c. of mercury at Paris (*i.e.* of 1013573

¹ *A Manual of the Steam-engine, &c.*, 4th ed. (1869), 307.

² *Pogg. Ann.* cxvi. (1862) 99, trans. *Phil. Mag.* [4] xxiv. (1862) 205.

³ *Bull. de la Soc. Philomat.* [7] i. (1877) 3.

dynes per sq. c.) is 0.000089578 g., the volume of 1 g. is

$\frac{1}{0.000089578}$ c.c., and, the coefficient of expansion under constant pressure being 0.003661, the expansion per degree is $\frac{0.003661}{0.000089578}$ c.c. and the external work done

$$\frac{0.003661 \times 1.013573}{0.000089578} = 41.329 \text{ megalergs:}$$

but the specific heat at constant pressure is

$$3.409 \times 41.55 = 141.644,$$

so that the specific heat at constant volume is

$$141.644 - 41.329 = 100.315.$$

Taking then as usual the atomic weight of hydrogen as unity, we have for all substances

$$a\bar{k} = 100$$

in round numbers.

Thus for iron, $a = 55.9$ whence $\bar{k} = 1.7889$; but

$$K = 0.11379 \times 41.55 = 4.7280,$$

and therefore the heat spent in internal and external work is

$$4.7280 - 1.7889 = 2.9391 \text{ megalergs:}$$

now the density of iron is about 7.75 and its coefficient of expansion about

$\frac{1}{18000}$, so that the external work done by a rise in temperature of 1 degree

is about $\frac{1}{7.75} \times \frac{1}{18000} \times 1.013573 = 0.000007$ megalergs, which is insensible:

thus the internal work requires 2.9391 megalergs of heat or 1.643 times that required for the mere change of temperature.

For lead $a = 206.4$ and $\bar{k} = 0.4845$; also

$$K = 0.03140 \times 41.55 = 1.3047,$$

and the external work done is equally negligible; hence the internal work is 0.8201 megalergs and requires 1.693 times the amount of heat spent in merely raising the temperature.

Similarly Hr. Woëstyn's law gives in the case of compounds

$$\bar{k} = \frac{\sum . na\bar{k}}{\sum . na} = 100 \frac{\sum . n}{\sum . na},$$

where n is the number of atoms in the compound of that element whose atomic weight is a .

Thus for carbon dioxide CO_2 ,

$$k = 100 \times \left(\frac{1+2}{1 \times 11.97 + 2 \times 15.96} \right) = 6.8353;$$

and, since $K = 0.2169 \times 41.55 = 9.0122$, the internal and external work is 2.1769 megalergs: but, the normal density at Paris of CO_2 being 0.001977414 and its coefficient of expansion under constant pressure being 0.003710, the external work done is $\frac{0.00371 \times 1.013573}{0.001977414} = 1.9017$, so that

the internal work is only 0.2752 megalergs, and requires $\frac{1}{25}$ th of the heat that merely increases the temperature.

For water H_2O we have similarly

$$k = 100 \times \left(\frac{2+1}{2 \times 1 + 1 \times 15.96} \right) = 16.704,$$

and therefore, as the external work is negligible, the heat spent in internal work when a gram of water at $\theta^\circ\text{C}$. is raised one degree is by § 10

$$41.55 (1 + 0.00022 \theta) - 16.704 = 24.846 + 0.00914 \theta \text{ megalergs.}$$

CHAPTER VI.

Degradation of Energy.

66. Available energy. We cannot convert into work the whole of an amount dH of heat at temperature t , as shewn in § 34: its practical value for useful transformation is

$$\frac{t-t_0}{t} dH \quad \text{or} \quad dH - t_0 \frac{dH}{t},$$

where t_0 is the lowest available temperature, being that of a refrigerator of dimensions and capacity for heat large enough to preserve its temperature sensibly constant when heat is given up to it: thus the work that can be got out of an amount $\int dH$ of heat by any process whatever is only

$$\int dH - t_0 \int \frac{dH}{t}. \quad (1)$$

When the process is reversible, this work has a maximum value which is called the *available* part of the heat-energy $\int dH$, as it represents the utmost amount that is capable under the given circumstances of being transformed into something more useful. It depends on temperature only, and is obviously the greater the higher the temperature of the body in which it is and the lower that of the refrigerator.

If this heat has been supplied at the expense of the intrinsic energy of a body which is surrounded by the refrigerator, and this energy has changed from E to E_0 in the process, we have

$$\int dH = E - E_0;$$

also we have $\int \frac{dH}{t} = \phi - \phi_0$

for reversible processes, where ϕ , ϕ_0 are the entropy in the initial and final states; and E_0 , ϕ_0 are perfectly determinable

when the final temperature t_0 and the final pressure p_0 are given: hence the part of the energy E of a body, enclosed in a medium of constant pressure p_0 and constant temperature t_0 , that *can* be usefully transformed, or the available energy of the body under the given circumstances, is

$$E - E_0 = t_0 (\phi - \phi_0). \quad (2)$$

Thus the greater the 'original entropy or the higher the final temperature, the less the available energy.

Professor Maxwell has shewn¹ this very elegantly by a diagram. Let A, B represent the initial and final states of the body: through A draw the isometric Aa and the isentropic $A\alpha$ meeting the axis of v at an infinite distance; through B draw similar lines $Bb, B\beta$, and also the isothermal BC : then the path-line AB representing the successive states of the body must lie below Aa as there is no body of higher temperature from which heat may be received, and it must lie above the isothermal BC

Fig. 27.

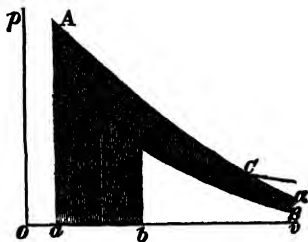


Fig. 27.

as t_0 is the lowest available temperature. The limiting path is therefore ACB , formed by the isentropic and isothermal: now by (2), § 33, the heat given out along this path, $t_0(\phi - \phi_0)$, is represented by the area $BCa\beta B$ and is obviously a minimum under the given conditions, and by (1), § 33, the loss of intrinsic energy $E - E_0$ is constant, being represented by the area $BbaAa\beta B$; hence the work done, which is equal to the difference $E - E_0 - t(\phi - \phi_0)$ and is represented by the area $ACBbaA$, is a maximum. Therefore the area $ACBbaA$ represents the available part under the given circumstances of the energy corresponding to the state A which is represented by $AavaA + \mathfrak{J}$.

Applying this result to our case in § 64, we shall obtain the greatest amount of work, while bringing back the heated gas to its initial condition,

¹ *Theory of Heat*, 4th ed. (1875), 187.

if we (1) allow it to expand without receiving or losing heat till its temperature falls from T to t_0 and its pressure from

$$p_0 \frac{T}{t_0} \text{ to } p_0 \left(\frac{T}{t_0}\right)^{\frac{\kappa}{\kappa-1}} = p_0 \left(\frac{t_0}{T}\right)^{\frac{1}{\kappa-1}},$$

and (2) then compress it at constant temperature till its pressure rises to the initial value p_0 : in the first process we shall gain an amount of work $k(T-t_0)$, and in the second we shall spend an amount

$$R t_0 \log_e \left(\frac{T}{t_0}\right)^{\frac{1}{\kappa-1}} = k t_0 \log_e \frac{T}{t_0} \quad (\text{since } \frac{R}{\kappa-1} = k);$$

hence the maximum amount of work which can be got out of the heated gas as it returns to its initial state is $k(T-t_0-t_0 \log_e \frac{T}{t_0})$, and as an amount of heat $k(T-t_0)$ has been communicated to the gas, the efficiency of the whole cyclical process is $1 - \frac{t_0}{T-t_0} \log_e \frac{T}{t_0}$. The maximum efficiency of a closed cycle in which the temperatures are those of the tube and of the gas in its initial state is $\frac{S-t_0}{S}$; now while this in our given case is 0.5, the efficiency of the other process is only 0.3475, or there is a greater sacrifice of heat to the refrigerator: hence if without expenditure of work we can continuously bring a body to a higher temperature than that of the source, it is simply because in place of sacrificing work we offer to the refrigerator a continuous and equivalent sacrifice of heat.

We may consider the more general case of an irregularly heated body in a perfectly non-conducting vessel of no capacity for heat: if all transferences of heat between the different parts are effected by perfect engines till the whole assumes an uniform temperature T , the work so done measures the available energy. Here is no infinite refrigerator for use with the perfect engines, but, as its only requisite is a constant temperature, we may employ instead any part of the substance whose temperature is T , such part on the whole receiving no heat during the processes as it serves also as source with regard to parts at lower temperatures. Let t be the specific heat of the mass dm at the point (x, y, z) for the particular circumstances of the change of temperature, being K , for example, if the change takes place under constant pressure: then as this mass is robbed of heat by the perfect engine it gives up to the

refrigerator the heat $dm \int_T^t \epsilon dt \frac{T}{t}$, the work done by the engine being $dm \int_T^t \epsilon dt (1 - \frac{T}{t})$. On the whole the refrigerator receives no heat, and therefore

$$0 = \int dm \int_T^t \epsilon dt \frac{T}{t} = \int dm \int_T^t \frac{\epsilon}{t} dt, \quad (3)$$

the integration extending all over the body: hence we find ;
The work done by all the engines is similarly

$$W = \int dm \int_T^t \epsilon dt (1 - \frac{T}{t}) = \int dm \int_T^t \epsilon dt, \quad (4)$$

by (3), and this represents the available energy of the body in its initial condition.

If Θ is the thermal capacity of the body and thus a function of the temperature, we have $\Theta = \int \epsilon dm$; hence (3) becomes

$$\int_T^t \frac{\Theta}{t} dt = 0 \quad \text{or} \quad \int_{t_0}^t \frac{\Theta}{t} dt = \int_{t_0}^T \frac{\Theta}{t} dt,$$

t_0 being a conveniently low temperature. The right-hand expression might be tabulated, the whole body being supposed for its calculation to be of uniform temperature: then T would be that value of t for which this expression is equal to the left-hand side of the equation. We should also have

$$W = \int_T^t \Theta dt.$$

If ϵ is independent of the temperature, (3) and (4) become

$$\int dm \epsilon \log \frac{t}{T} = 0 \quad \text{or} \quad T = 10^{\frac{\int \epsilon \log t dm}{\int \epsilon dm}}$$

$$W = \int dm \epsilon (t - T).$$

If the body is also homogeneous, ϵ is the same for every part of it, and we get the further simplifications

$$T = 10^{\frac{1}{M} \int dm \log t},$$

$$W = \epsilon (\int t dm - M T),$$

M being the whole mass. If the body consists of masses m_1 at

temperature t_1 , m_1 at temperature t_2, \dots of the same homogeneous material for which τ is independent of t , these equations become

$$T = 10^{\frac{\sum m \log t}{\sum m}} = (t_1^{m_1} t_2^{m_2} \dots)^{\frac{1}{\sum m}},$$

$$W = \tau (\sum m t - T \sum m).$$

This method was first given by Sir W. Thomson¹ in 1852: the above equations are his, as slightly simplified in expression by Professor Tait.

The still more general case we might consider of several irregularly heated bodies at different pressures in the non-conducting enclosure: the final uniform state as to pressure and temperature to which the system may be brought when all transferences of heat are effected by perfect engines is the same in whatever way or order the engines act: hence we may bring each body to a state of uniform temperature, and then the system to an uniform temperature, whence the theorem—*the available energy of a system is the sum of the available energies of each of its parts together with that of the system consisting of these parts each with its individual available energy exhausted.*

The equations in this case are of the same form as the above: now equation (3) indicates that the entropy of the system must remain unchanged if the maximum amount of work is to be obtained, and thus Professor Maxwell's proposed method is suggested:—

(a) Bring each of the bodies without communication of heat to what will be the final uniform temperature of the system, this temperature being calculated by (3): the entropy of each is unchanged by this process.

(b) Let those bodies that exert the greatest pressures compress the others, the process being conducted so slowly that there is no sensible variation of temperature in any part: as communication of heat occurs only between bodies of the same temperature, the total entropy is unchanged.

The entropy of the system being thus constant throughout

¹ *Proc. R. S. E.* iii. (1852) 139, or *Phil. Mag.* [4] iv. (1852) 304, and [4] v. (1853) 102.

the whole process, the total change in energy of the system will measure the work obtained, and will therefore represent the available energy. These operations might have been suggested by a consideration of the above graphical method.

67. Dissipation of energy. We know energy under many different forms which are of different orders of usefulness to us:—thus it is most useful to us as mechanical effect, and as heat of high temperature it is more useful than as heat of low temperature: we may therefore class one form as higher than another. One form may in general be transformed into another either wholly or in part¹, but subject to what may be called the Law of the Degradation of Energy, viz.—*all transformations are accompanied by a degradation of energy, i.e. by a transformation of energy to a less useful form.*

This was first recognized by Sir W. Thomson² in the case of heat and mechanical effect, and he called it the Law of the Dissipation of Mechanical Energy. The former term is better, both as indicating what has become of the energy—that it is not destroyed but present in a lower form—and also as more general. His reasoning, which depends on Carnot's principle, may thus be exhibited. We can always transform mechanical energy entirely into heat, the transformation being to a lower form; but the work that is obtained from an amount of heat-energy $\int dH$ by any process is, by (1), less than $\int dH$ by the quantity

$$t_0 \int \frac{dH}{t},$$

where t_0 is the lowest available temperature, and this expression therefore represents the energy dissipated. If the process is reversible, this dissipation is a minimum, and it is then equal to $t_0(\phi - \phi_0)$, where ϕ , ϕ_0 are the entropy of the body from which the heat is taken in its initial and final states. If the process is not reversible, the dissipation is greater, and there is an actual *waste* of availability equal to

$$t_0 \left(\int \frac{dH}{t} + \phi_0 - \phi \right).$$

¹ See Professor Balfour Stewart's *Conservation of Energy*.

² *Proc. R. S. E.* iii. (1852) 139, or *Phil. Mag.* [4] iv. (1852) 304, and [4] v. (1853) 102.

From the conditions of reversibility in § 51 we see that a reversible process is impracticable; for it is impossible to prevent either friction in the parts of a machine or thermal communication between parts at different temperatures by conduction or radiation: therefore this waste is not preventible.

It is found that all other forms of energy tend to be transformed into the energy of diffused heat, but that a re-transformation cannot occur except on the expenditure of work or a sacrifice of heat to a refrigerator—in either case a loss of availability: hence dissipation accompanies every transformation of energy, and as every operation in nature consists in such transformations, it follows that the energy of the universe, while remaining constant in quantity, is gradually being dissipated or degraded; its final state must therefore be one of uniformly diffused heat. Dissipated energy is thus energy that we cannot direct at will, such as molecular energy: could we follow each atom in its course and seize it at pleasure, there would be no dissipation.

In the general case of many irregularly heated bodies in a non-conducting enclosure of no capacity for heat, the effect of radiation and conduction is to diminish differences of temperature and thus the available energy of the system: but equation (4) does not give the dissipation when the temperature has become uniform, for the final temperature will in this case be greater than T , since no heat has been removed in the form of work done, as there supposed. The real conditions are these: if T' is the final uniform temperature, the heat gained by a particle at temperature T' from all the others by radiation and conduction is on the whole zero, or

$$\int dm \int_{T'}^t \epsilon dt = 0, \quad (5)$$

whence T' : also the work that could have been gained in transferring by perfect engines to this particle all the heat that has left the others is

$$W' = \int dm \int_{T'}^t \epsilon dt \left(1 - \frac{T'}{t}\right) = -T' \int dm \int_{T'}^t \frac{\epsilon}{t} dt, \quad (6)$$

by the preceding equation, and this represents the dissipation.

If the system is homogeneous and ϵ is independent of the temperature, these equations become

$$T' = \frac{1}{M} \int t dm,$$

$$W' = \epsilon T' (M \log_e T' - \int dm \log_e t).$$

68. Possibility of restoring lost availability. Professor Rankine suggested¹ that it might be possible to reconcentrate, as it were, dissipated energy or to restore to it availability for useful transformation: for as diffused heat ultimately takes the radiant form (the ether not being thereby raised in temperature as it is perfectly diathermanous), this radiant energy on reaching the confines of space may possibly be totally reflected and ultimately reconcentrated into foci of such intensity 'that, should a star (being at that period an extinct mass of inert compounds) in the course of its motions arrive at that part of space, it will be vaporized and resolved into its elements, a store of chemical power being thus reproduced at the expense of a corresponding amount of radiant heat.' This hypothesis really assumes that at a focus of concentrated rays a body may be heated to a temperature higher than that of the bodies emitting the rays, and is therefore contrary to our fundamental axiom that heat cannot of itself pass from a colder to a warmer body.

Hr. Clausius has further refuted this hypothesis by a detailed discussion of the theory of radiation²: he gives the following summary of his principal results:—

1. 'To bring the effects of ordinary radiation, without concentration, into harmony with the principle that heat cannot of itself pass from a colder to a warmer body, it is necessary to assume that the intensity of emission from any body depends not only upon its own constitution and temperature, but also upon the nature of the surrounding medium; in fact the intensities of emission of one and the same body in different

¹ *B. A. Rep.* (1852) ii. 12, or *Phil. Mag.* [4] iv. (1852) 358.

² *Pogg. Ann.* cxxi. (1864) 1.

media must be inversely proportional to the squares of the velocities with which rays are therein propagated, or, in other words, directly proportional to the squares of the coefficients of refraction for these media.

2. 'If this assumption as to the influence of the surrounding medium be correct, the above principle must obtain, not only for ordinary radiation, but also when the rays become concentrated in any manner whatever through reflexions and refractions; for although concentration may change the absolute magnitudes of the quantities of heat which two bodies radiate to each other, it cannot alter the ratio of these magnitudes.'

We can easily shew the latter in the case of reflexion. Let radiation leaving the small area da of A at an angle i to the normal fall at a distance r on the small area da' of B at incidence i' ; then the solid angle of the incident cone of rays is $\frac{da' \cos i'}{r^2}$, and, e being the normal radiation of A , the total amount of radiation falling on B from A is

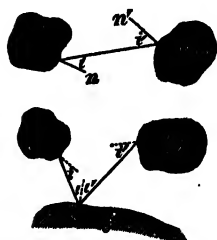


Fig. 28.

$$\iint e \cos i \, da \cdot \frac{da' \cos i'}{r^2};$$

similarly, if e' is the normal radiation of B , the total radiation falling on A from B is

$$\iint e' \cos i' \, da' \cdot \frac{da \cos i}{r^2},$$

and the ratio of these two quantities is obviously $\frac{e}{e'}$. Now suppose the rays from A first reflected by the surface C before falling on B : then the radiation from the small area da of A falling at a distance ρ upon a small area da of C at incidence i is by the foregoing

$$e \, da \cos i \cdot \frac{da \cos i}{\rho^2} \quad \text{or} \quad e \, d\omega \, da \cos i,$$

where $d\omega \equiv \frac{da \cos i}{\rho^2}$ is the solid angle subtended at the ele-

ment da by the small area da ; and similarly the radiation from the small area da' that falls upon this same element da is $e' d\omega' da \cos i'$: if then da is the element of C at which the rays from da are reflected to da' , so that one is the image of the other, the laws of reflexion give $d\omega = d\omega'$ and $i = i'$, and therefore the ratio of the radiations from da to da' and from da' to da is $\frac{e}{e'}$, which, being constant, is also the ratio of the whole radiation from A to B to the whole radiation from B to A . Thus the ratio is unaltered by the reflexion. It is to be noticed that the radiation which falls upon B in the two cases does not necessarily proceed from the same parts of A , and *vice versa*.

CHAPTER VII.

Comparison of Theory with Experiment.

APPLICATION TO GASES.

OUR results have hitherto been expressed in terms of temperature, on Sir W. Thomson's absolute scale: in order to make use of actual experiments we must determine the relation between this scale and those in ordinary use. This relation has been deduced from the behaviour of gases during expansion.

69. Dr. Joule's experiments¹. Two copper vessels, of capacity 2196 and 2237 c.c. respectively, the first exhausted of air and the second containing air at about 22 atmospheres pressure, were connected together by a brass pipe provided with a stopcock and placed together in a tinned-iron can with double walls containing 7484 grams of water at 14.9°C. ; the stopcock was then opened so that the air expanded into the empty vessel, but no variation of the temperature of the water was observed to result (even though the thermometer used read to $\frac{1}{3880}$ degree c.) after the necessary corrections were made for radiation and the warmth produced by stirring the water to equalize its temperature throughout: Dr. Joule therefore concluded that 'no change of temperature occurs when air is allowed to expand without developing mechanical power' (*i.e.* doing external work).

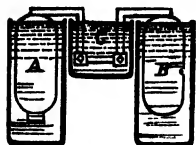


Fig. 29.

To analyze the above experiment Dr. Joule placed the vessels in separate cans of water and the stopcock in a third; the air, initially under 20.7 atmospheres pressure, caused a fall of 0.595 degree c. per kilogram of water in A which contained all the air at first and a rise of 0.600 degree c. per kilogram in B, a rise of 0.078 degree c. per

¹ *Phil. Mag.* [3] xxvi. (1845) 376.

kilogram further occurring in *C*. This confirms the above result, the slight redundancy of heat being due to the partial heating of the cooled air as it passed from *A* to *C* through that part of the pipe which could not be immersed in water.

If this is so, the internal work during the expansion of air is zero, or by § 58

$$t^2 \frac{\partial}{\partial t} \cdot \frac{w}{t} = 0,$$

whence, if \mathfrak{V} represents a function of v ,

$$w \equiv \int p dv = t \mathfrak{V}, \quad p = t \mathfrak{V}',$$

and by (22), § 57,

$$E - E_0 = k (t - t_0),$$

k being also by (13), § 54, equal to k since $\frac{\partial^2 w}{\partial t^2} = 0$. But M. Regnault's experiments shew that the specific heat of air referred to the *c.* scale on the air-thermometer \mathcal{K} is constant, so that

$$E - E_0 = \mathcal{K} (\tau - \tau_0) :$$

but if t, τ refer to the temperature of boiling water under normal pressure and t_0, τ_0 to the temperature of melting ice,

$$t - t_0 = \tau - \tau_0 = 100 ;$$

therefore $\mathcal{K} = k$, and we have generally

$$\tau = t + (\tau_0 - t_0).$$

But $\tau_0 = t_0 = 0$ at the temperature corresponding to absolute deprivation of heat, so that $\tau = t$, or absolute temperature is the same as that measured on the air-thermometer.

The degree of exactness in the above experiments may thus be determined. In the first the mass of air used was

$$2237 \times 22 \times \frac{274}{288 \cdot 9} \times 0 \cdot 0012932 = 60 \cdot 355 \text{ grams,}$$

and the water-equivalent of the calorimeter-vessels and water was about 9750 grams: now a variation of 1 degree *c.* in 9750 g. of water requires the same amount of heat as a variation of 1 degree *c.* in $\frac{9750}{0 \cdot 2389} = 40812$ g. of air, or a variation

through $\frac{40812}{60 \cdot 355} = 676$ degrees *c.* of the amount of air used in the experiment; thus, as the thermometer immersed in the

water read to only $\frac{1}{380}$ degree c., it would not be affected by a variation in the temperature of the air less than $\frac{570}{380} = 1.88$ degree c. Dr. Joule's conclusion is not therefore absolutely established by these experiments: in fact we are going to shew that internal work to a slight extent does occur during the variations in the density of real gases. The absolute and air-thermometer scales are not therefore identical, but differ very slightly from each other.

*We should not get any better result by placing the thermometer in the vessel instead of the air, for before an accurate reading of the temperature of the air could be made, the air would have taken the temperature of the walls of its enclosure. Such an experiment was performed by M. Gay Lussac¹, who found a fall of temperature in the one vessel and a rise in the other, but could make no quantitative measures.

70. M. Hirn's experiment. A more delicate experiment² was made by M. Hirn in 1865. A long copper cylinder was divided into two equal compartments by a membrane, and an open-air oil-manometer, provided with a stopcock, was fitted to one of them: both compartments were then filled with gas at atmospheric pressure and the manometer stopcock turned, the oil being at the same level in both arms. The gas was then pumped from one compartment into the other, and, when the pressures became $\frac{1}{2}$ and $1\frac{1}{2}$ atmospheres respectively, the membrane was broken by the fall of a leaden bullet and the manometer simultaneously opened. No displacement in the manometer levels was observed and therefore no variation of temperature revealed.

Now a depression of 1 mm. of the oil in the guage corresponds to a difference in pressure of 0.02 c. of oil or (the density of oil being 0.8) of $\frac{0.02}{76} \times \frac{0.8}{13.596} = \frac{1}{6458}$ atmosphere; and since, when the volume is constant, $p \propto t$ or $\delta t = \frac{t}{p} \delta p$, the change of temperature corresponding to this change of

¹ *Mém. d'Arcueil*, i. (1807) 180.

² *Théorie mécanique de la Chaleur* (3^{ème} éd.), i. 298.

pressure when $p = 1$ and $t = 285.7$ (or 12° c.), as in the above experiment, is $\frac{285.7}{1} \times \frac{1}{6458} = 0.044$ degree. A depression of 0.01 c. could easily be observed, even if it lasted scarcely a second, and therefore a variation of 0.044 degree would have shewn itself, if it had occurred.

The delicacy of this arrangement is of little avail, M. Hirn being convinced by numerous experiments that 'even when the gas had fallen through 1 or 2 degrees below the initial temperature after the membrane was broken, it would be heated so quickly at the expense of the walls of the cylinder that the manometer would not have time to shew an appreciable fall of temperature.'

71. Sir W. Thomson's method. A still more delicate method¹ is due to Sir W. Thomson, who proposed in 1851 to replace the vessels in Dr. Joule's experiments by long spiral tubes, still retaining the stopcock or its equivalent, a partition with a small orifice, and to force air continuously but slowly through the whole at constant temperature. If there is any variation of temperature of the air in passing through the orifice, the initial temperature may perhaps be again attained only after the passage through a considerable length of the second spiral, which must therefore be long enough to ensure this. The first spiral is required merely to fix the temperature of the entering air, and the process is to be so managed that the pressures of the entering and issuing air do not vary. The velocity of issue is to differ very little from that of entrance, so that the pressure is employed entirely in overcoming the resistance encountered by the air, and not in giving it kinetic energy.

Let p, v characterize the entering and p', v' the issuing air when the motion has become steady—that is, when equal amounts of air enter and leave the tube. In general the fluid friction in the *rapids* (the orifice and its neighbourhood) will give rise to heat, and at the same time heat may be required for the work of expansion; the balance therefore will be

¹ *Trans. R. S. E.* xx. (1851) 294.

absorbed by the water in which the second spiral is immersed, and may thus be measured. The heat that results from the friction of the particles against each other and the edges of the orifice is equal to the mechanical work that would have been done if the expansion had occurred without any friction; it can thus be measured by our supposing the pierced partition removed and a series of moveable pistons without inertia substituted, between each successive pair of which unit-mass of air

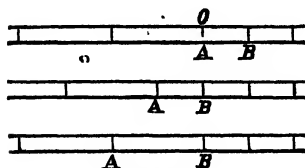


Fig. 30.

is enclosed, their motion being such that each piston *A* moves past the position of the orifice *O* till the next piston *B* reaches *O*, the volume between them being constantly *v*, that *B* then remains at rest till by the continued motion of *A* the volume

between them has become *v'*, that they then move forward with this volume unaltered. During these two processes for each pair of pistons the work done is $(p-p')v$ and $\int_v^{v'} (p-p') dv$ respectively, the *p* in the integral being variable: hence their sum

$$\int_v^{v'} p dv + pv - p'v'$$

is equal to the heat caused by the fluid friction. Again, during the expansion at constant temperature heat equal to $\int l dv$ will be absorbed; but by § 48 the general expression for *l* is $\frac{1}{\mu} \frac{\partial p}{\partial t}$, where μ is Carnot's function and *t* is the temperature measured on any scale whatever; supposing therefore the scale to be that of the air-thermometer and consequently replacing *t* by τ_x we have for the heat absorbed

$$\frac{1}{\mu} \int_v^{v'} \frac{\partial p}{\partial \tau} dv,$$

μ being placed outside the integral as it is a function of the temperature. The heat taken up by the calorimeter is thus

$$-H = \int_v^{v'} p dv + pv - p'v' - \frac{1}{\mu} \int_v^{v'} \frac{\partial p}{\partial \tau} dv,$$

+ H denoting as usual the heat *taken in* by the air as it changes state; and whatever changes of temperature there may actually be of the air in or near the orifice, this expression will give rigorously the total quantity of heat emitted by that portion of the tube which contains the orifice and the whole of the second spiral during the passage of a volume v through the first spiral, or v' through any portion of the second spiral where the temperature is sensibly τ . Now absolute temperature is defined as the reciprocal of Carnot's function, and therefore

$$t = \frac{\int_v^{v'} p dv + pv - p'v' + H}{\frac{\partial}{\partial \tau} \int_v^{v'} p dv} \quad (1)$$

We know not the true relation between p , v , and τ , or we could find by this equation the *exact* relation between temperature on the absolute and air-thermometer scales: but the approximate formula

$$pv = R\tau$$

gives the result

$$t = \tau + \frac{H}{R \log_e \frac{p}{p'}}, \quad (2)$$

which is very approximately true.

Sir W. Thomson proposed¹ also to modify this experiment and to determine by a thermopile whether cooling or heating accompanies expansion, one set of the solderings being fixed within the tube on one side of the orifice and the other set within the tube on the other side, both sets being placed out of the rush of air. Supposing as before that the air is flowing gently even though the pressure may be very high (the pressure being thus employed merely in overcoming the resistance introduced into the tube by the pierced partition), there will be a section A of the tube not far distant from the orifice, everywhere behind which (*i. e.* in a direction away from the orifice) the pressure, specific volume and temperature are constant and represented by p , v , τ , and



Fig. 31.

¹ *Trans. R. S. E.* xx. (1851) 481.

there will also be on the other side of the orifice and near to it a section B , everywhere behind which the pressure, specific volume and temperature are constant and represented by p' , v' , τ' , the rapids being between these sections: now in forcing unit-mass of air across the section A we spend work equal to pv , but, as unit-mass simultaneously crosses the section B , doing work equal to $p'v'$, we communicate to it energy only equal to $pv - p'v'$. It may also absorb heat H from surrounding bodies, and it may lose part of its energy Σ in producing sound as it passes through the rapids: thus it experiences an increase of intrinsic energy $H - \Sigma + pv - p'v'$, or, if E , E' denote its intrinsic energy at and behind the sections A and B ,

$$E' - E = H - \Sigma + pv - p'v'. \quad (3)$$

In the case wherein loss and gain of heat are prevented and the energy of sound vibrations is negligible the equation becomes

$$E + pv = E' + p'v',$$

or

$$d.(E + pv) = 0: \quad (4)$$

but, accenting the thermal capacities to shew that they are expressed in terms of temperature on the air-thermometer, we have generally

$$\begin{aligned} d.(E + pv) &= (dE + p dv) + v dp = K' d\tau + (L' + v) dp \\ &= K' d\tau - \left(\frac{1}{\mu} \frac{\partial v}{\partial \tau} - v\right) dp, \end{aligned}$$

since by (7), § 16,

$$L' = l' \frac{\partial v}{\partial p}, \text{ and also } l' = \frac{1}{\mu} \frac{\partial p}{\partial \tau}, \quad \frac{\partial v}{\partial p} \cdot \frac{\partial p}{\partial \tau} = - \frac{\partial v}{\partial \tau}.$$

Hence in this case, when H is zero,

$$\frac{1}{\mu} \frac{\partial v}{\partial \tau} - v = K' \left(\frac{\partial \tau}{\partial p}\right)_\phi,$$

or, as absolute temperature is the reciprocal of μ ,

$$t = \frac{v + K' \left(\frac{\partial \tau}{\partial p}\right)_\phi}{\frac{\partial v}{\partial \tau}}. \quad (5)$$

Now the approximate formula $p v = R \tau$ gives

$$\frac{\partial v}{\partial \tau} = \frac{R}{p} = \frac{v}{\tau};$$

and thus

$$\begin{aligned} t &= \tau + \frac{K'}{R} p \left(\frac{\partial \tau}{\partial p} \right)_{\phi} \\ &= \tau + \frac{K'}{R} \left(\frac{\partial \tau}{\partial \log_e p} \right)_{\phi}; \end{aligned}$$

or substituting differences for differentials, since they are small, we get

$$\begin{aligned} t &= \tau + \frac{K'}{R} \cdot \frac{\mathfrak{S}}{\log_e p' - \log_e p} \\ &= \tau - \frac{K' \mathfrak{S}}{R \log_e \frac{p}{p'}}, \end{aligned} \tag{6}$$

\mathfrak{S} being the resulting increase of temperature (measured on the air-thermometer) during the change of pressure from p to p' . This equation is approximately the same as (2); the signs of the second terms of the right-hand expressions are the same since, if heat is absorbed by the air or H positive, there must have been a cooling or \mathfrak{S} negative.

72. Dr. Joule and Sir W. Thomson's experiments. The latter of these proposed methods has been extensively used by Dr. Joule and Sir W. Thomson working together¹, but the pierced partition was replaced by a porous plug, as with a mere orifice a thermometer placed in the issuing air underwent different actions according to its position and shape. The nozzle finally adopted was attached to the upright end of the long spiral pipe aa of copper through which the air was forced: it consisted of a perforated metallic disc b resting on a shoulder within the pipe, on which stood a short piece of india-rubber tube cc enclosing a silk plug d , that was kept in a compressed state by the upper perforated metallic plate e , against which the metallic tube ff was pressed down by means of the screw gg : a tube of cork hh was placed within ff to

¹ *Phil. Mag.* [4] iv. (1852) 481; *Phil. Trans.* cxliii. (1853) 357, cxliv. (1854) 321; *Proc. R. S. x.* (1860) 502; *B. A. Rep.* (1861) ii. 83; *Phil. Trans.* clii. (1862) 579.

protect the bulb of the thermometer from the effects of a too rapid conduction of heat from the bath, and cotton wool was packed loosely round the bulb so as to distribute the flowing air as evenly as possible : the tube *ii*, attached to the nozzle by india-rubber tubing, was of glass, in order to permit readings of the thermometer. This nozzle obviated the *rapids* and caused the work done by the expanding air to be immediately spent in friction without generation, even temporarily, of ordinary kinetic energy or of sound. The difference between the pressures on each side of the nozzle was varied by altering the amount of silk or cotton compressed in the plug.



Fig 32.

The issuing air was always found to be cooled by the expansion, but several precautions were found necessary for quantitative measurement : thus (1) the cooling was greater at first owing to necessary drying of the material (silk or cotton) of the plug : (2) oscillations of temperature were caused by the intermittent action of the pump, from which also particles of sperm-oil or of dust were carried over ; the air was therefore made to pass through a box with perforated caps and stuffed with cotton wool before entering the spiral : (3) a series of fluctuations in the temperature occurred on opening the stopcock which allowed the air to pass through the plug ; the cooling effect arising from the instantaneous increase of pressure caused a depression at first which was soon overtaken by a larger heating effect arising from the compression of the air in the spiral, and though these disturbances soon ceased owing to the air reaching the temperature of the bath by contact with the good conducting copper pipe, yet other and longer continued fluctuations were caused by its contact with the badly conducting walls of the plug, the temperature of which was long in becoming steady ; the pump was therefore allowed to work for a considerable time before any observations were recorded. The correction for conduction of heat through the plug was determined by experiments in which the difference between the

temperatures of the bath and the air was made very great, and it was considered directly proportional to the difference of temperature and inversely to the quantity of fluid transmitted in a given time.

A first series of experiments shewed that $\frac{\mathfrak{S}}{\log_e \frac{p}{p'}}$ increases with $\frac{p}{p'}$, and we must therefore use the more complete formula

$$t = \tau + \frac{pv - p'v' - K'\mathfrak{S}}{R \log_e \frac{p}{p'}} \quad (7)$$

obtained from (1) by evaluating the integrals only on the supposition that $pv = R\tau$ and substituting $-K'\mathfrak{S}$ for H .

A second series then shewed that for a constant temperature of the bath the cooling $-\mathfrak{S}$ varies directly as the difference of the pressures $p-p'$ and decreases as the temperature rises, the values of $\frac{\mathfrak{S}}{p-p'}$, when pressure is measured in c. g. s. atmospheres, being

Air	CO ₂	H
-0.255 at 17.1°	-1.207 at 12.8°	-0.021 at 10°
-0.203 „ 91.6°	-1.144 „ 19.1°	
	-0.693 „ 91.5°	

the temperatures being expressed on the centigrade scale. In one experiment on air at 16° c. the cooling was 0.676 degree when $p = 3.6891$, $p' = 1.0053$: now Hr. Schröder van der Kolk's reduction¹ of M. Regnault's experiments on the compressibility of gases gives for air at 4.42° c.

$$\frac{pv}{p_0 v_0} = 1.00127 - 0.00172 p + 0.000041 p^2,$$

p_0 corresponding to 76 c. of mercury at Paris; hence supposing

¹ *Pogg. Ann.* cxvi. (1862) 429.

that this equation holds good at 16°C. (which cannot be far from the truth) and substituting $R\tau_0$ or

$$2.8725 \times (272.8 + 16) = 829.578$$

for $p_0 v_0$ (see § 63) we have

$$pv = 830.628 - 1.4266p + 0.033912p^2,$$

and thus in the above case $pv - p'v' = -3.4015$; also (§ 63) $R = 2.8725$, $K' = 9.9263$, so that $K' \theta = -6.7102$,

$$R \log_e \frac{p}{p'} = 3.7345;$$

therefore $t = 288.8 + \frac{3.3087}{3.7345} = 289.69$, and, as the value of

t at 0°C. must be, within a very small fraction, less by 16 than its value at 16°C. , the absolute temperature corresponding to 0°C. is 273.69° . The result of all the experiments leads to the conclusion that absolute zero temperature is -273.7°C. , and gives the following comparison of the absolute scale with that of an air-thermometer in which air is employed of relative density d , the standard density being that of air at 0°C. under a pressure of one c. g. s. atmosphere (which is 0.0012759 grams per cubic centimetre).

Temperature by absolute scale measur- ed from 0°C. $t - 273.7$ "	Temperature centigrade on air- thermometer. $\theta = 100 \frac{p_1 - p_{m-1}}{p_{m-1} - p_{m-2}}$	Temperature by absolute scale measur- ed from 0°C. $t - 273.7$	Temperature centigrade on air- thermometer. $\theta = 100 \frac{p_1 - p_{m-1}}{p_{m-1} - p_{m-2}}$
0	0	0	0
0	0	160	$160 - 0.0970 \times d$
20	$20 + 0.0294 \times d$	180	$180 - 0.1363 \text{ ,,}$
40	$40 + 0.0398 \text{ ,,}$	200	$200 - 0.1772 \text{ ,,}$
60	$60 + 0.0361 \text{ ,,}$	220	$220 - 0.2202 \text{ ,,}$
80	$80 + 0.0220 \text{ ,,}$	240	$240 - 0.2627 \text{ ,,}$
100	100	260	$260 - 0.3099 \text{ ,,}$
120	$120 - 0.0280 \text{ ,,}$	280	$280 - 0.3562 \text{ ,,}$
140	$140 - 0.0607 \text{ ,,}$	300	$300 - 0.4030 \text{ ,,}$

A third series of experiments shewed that the cooling per megadyne of difference between the initial and final pressures is inversely proportional to the square of the initial temperature, or

$$-\frac{S}{p-p'} = \frac{a}{t^2}, \quad (8)$$

where a is a constant, the value of which for air is about 20337 and for CO_2 about 102571.

Hence the characteristic equation for permanent gases may be determined from

$$t \frac{\partial v}{\partial t} - v = K \left(\frac{\partial t}{\partial p} \right)_\phi,$$

an equation obtained in the same manner as (5); for on substituting from (8) we have

$$t \frac{\partial v}{\partial t} - v = K \frac{a}{t^3},$$

whence on integration

$$\frac{v}{t} = \psi(p) - \frac{Ka}{3t^3},$$

since K is constant. The function must be of the form $\frac{R}{p}$, where R is constant, as Boyle's law is very approximately followed by gases, especially when t is great; thus we obtain

$$\frac{pv}{t} = R - \frac{Ka p}{3t^3}. \quad (9)$$

This formula was also found by Professor Rankine by another method¹ and shewn to give results agreeing most satisfactorily with experiment.

The further results of these experiments are the following values of $\frac{S}{p-p'}$ for different gases:—

O	N	H
−0.317 at 8.7°	−0.305 at 7.2°	+0.089 at 6.8°
−0.165 „ 93°	−0.187 „ 91.7°	+0.046 at 90.2°

¹ *Phil. Trans.* cxliv. (1854) 337.

It will be noticed that whereas a cooling was observed before during the expansion of hydrogen, the real effect is shewn by these more exact experiments to be a heating, and this is doubtless connected with the compressibility of H being less than Boyle's law would give: and further, the cooling effects for CO_2 , N , air, are in descending order of magnitude, as we should expect from their coefficients of dilatation being in the same order.

The experiments also shewed that a mixture of gases invariably gives a smaller cooling effect than the average effect of the pure gases.

Professor Rankine found¹ that the Centrifugal Theory of Elasticity—a generalization of the theory of molecular vortices—indicates that the characteristic equation of an imperfect gas may be represented by the formula

$$\frac{pv}{p_0 v_0} = \frac{t}{t_0} + a_0 - \frac{a_1}{t} - \frac{a_2}{t^2} - \dots,$$

where a_0, a_1, \dots are functions of the density $\frac{1}{v}$ which must be determined by experiment. Dr. Joule and Sir W. Thomson have used² the simpler formula

$$pv = Rt - \left(a - \frac{\beta}{t} + \frac{\gamma}{t^2} \right) \frac{1}{v},$$

where R, a, β, γ are constants, the values of which in the case of air they find to be $R = 2.8659$, $a = 777.386$, $\beta = 844560$, $\gamma = 214325840$.

73. M. Cazin's experiments. M. Cazin in 1867 employed³ an apparatus which allowed him to examine the state of a gas at any moment of its passage from one reservoir to another at approximately constant temperature. Two metal reservoirs A and B , of capacity 8923 and 33805 c.c. respectively, were connected together by a large brass stopcock C ; they were connected also to a force pump D and to separate

¹ *Trans. R. S. E.* xx. (1853) 581.

² *Phil. Trans.* cxliv. (1854) 360.

³ *Ann. de ch. et de phys.* [4] xx. (1870) 251, trans. *Phil. Mag.* [4] xl. (1870) 81, 197, 268.

open-air manometers *E* and *F*: to preserve their temperature constant they were provided with double walls between which a constant circulation of water was maintained. Air having been pumped from *B* into *A* the stopcock was opened, and the variation of pressure in *B* during the motion of the gas was measured by a special sensitive open-air manometer *G*, in which hydrogen sulphate was the indicating liquid; this manometer was put in

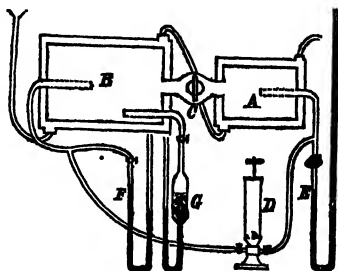


Fig. 33.

connection with *B* at a known interval (which was varied) after the opening of *C*, and the times at which different observations were made or operations performed were registered by electric action on a chronograph. The inertia of the liquid prevented the manometer *G* from indicating the exact pressure at each moment, but a large series of experiments enabled M. Cazin to draw an approximate curve of pressures. His results are—

When a reservoir containing compressed gas is placed in communication, by a large orifice, with a reservoir containing the same gas rarefied, equality of pressure establishes itself very quickly in the two reservoirs (0.1 second). When equality of pressure commences, the velocities acquired have not completely disappeared. At this instant the gas in the first reservoir is cooler than at first, as it has done mechanical work: on the contrary, the gas in the second reservoir has been heated, mechanical work having been done in compressing it; but a part only of the kinetic energy produced during the efflux has been transformed into heat. While however this transformation continues the pressure increases, and when the motion has ceased the heat that has disappeared from the first reservoir is greater than that which has appeared in the second: equilibrium of temperature is quickly brought about by conduction from or through the walls, and thus, on the whole, heat

is absorbed from the outside. If the walls were impermeable by heat, the equilibrium would be established by exchanges between the hot and cold parts, but the final temperature would be less than the initial.

74. Specific Heat of gases at constant volume. In § 65 we have shewn that k , which is constant for each substance in all states of aggregation, is equal to the specific heat at constant volume of the substance when it is in the perfectly gaseous state, that is, a highly superheated vapour: hence a determination of this specific heat of gases is necessary. Hitherto no direct determinations have been made, and indeed they scarcely appear possible, since the mass of the gas enclosed in any vessel is so small relatively to that of the vessel that there is no appreciable difference in the heat necessary to produce a given thermal effect in the vessel, whether it is vacuous or full of gas. The determination can however be made indirectly by finding the value of κ , the ratio of the specific heat at constant pressure to the specific heat at constant volume, and two methods have been employed, (A) the observation of the thermal effects that accompany the adiabatic expansion and compression of gases, (B) the comparison of the observed velocity of sound with the value given by a theoretical formula.

A. If a gas is confined in a vessel which is incapable either of communicating heat to the gas or receiving heat from it, then, when compression or expansion takes place, its pressure, specific volume, and temperature change from p_0, v_0, t_0 to p, v, t , so that by (62), § 63,

$$\left. \begin{aligned} \kappa &= \frac{\log p - \log p_0}{\log v_0 - \log v} \\ &= \frac{\log t - \log t_0}{\log v_0 - \log v} + 1 \\ &= \frac{\log p - \log p_0}{\log p - \log p_0 - \log t + \log t_0} \end{aligned} \right\} \quad (10)$$

If then we can determine the change of any two of the three quantities, we can at once find κ : as however no substance is known which will not conduct heat the experiment is in this

form impossible, unless the compression or expansion is effected so rapidly that the heat lost or gained by the gas is negligible; and, though in this case the time is too short for us to measure the thermal effect or the changes of pressure and temperature, yet by observing the final state of the gas we may estimate them.

(1) MM. Clément and Désormes¹ used a 20-litre glass globe closed by a large stopcock *A* and connected with a vertical glass tube *B* dipping into water which acted as a manometer. The air within the vessel was partially rarefied by an air-pump which could be connected with *C*; *A* was then opened for half a second, in which time the pressure was raised to that of the atmosphere by the entrance of air; the incoming air had however by compressing the air already there raised its temperature, and as this cooled again to the surrounding temperature the pressure diminished. Let Π be the atmospheric pressure, v the specific volume of the air, t its temperature, p_0 its original and p its final pressure: by the adiabatic compression the pressure of the air is increased from p_0 to Π ; also the specific volume is diminished in the proportion of p_0 to p , or

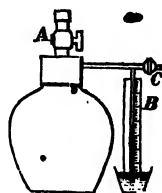


Fig. 34.

$$\log v_0 - \log v = \log p - \log p_0,$$

since p is the pressure of the air after regaining its initial temperature: hence

$$\kappa = \frac{\log \Pi - \log p_0}{\log p - \log p_0}.$$

In one of the experiments

$$\Pi = 1.0136, \quad p_0 = 0.9953, \quad p = 1.0088,$$

whence $\kappa = 1.3524$.

(2) MM. Gay Lussac and Welter² altered this experiment by initially introducing compressed air into the vessel and then allowing it to escape adiabatically till the pressure in the vessel became equal to that of the atmosphere: the expansion having

¹ *Journal de Physique*, lxxxix. (1819) 428.

² *Ann. de ch. et de phys.* [1] xix. (1821) 436.

136. *Comparison of Theory with Experiment.*

cooled the air, its pressure is finally greater than that of the atmosphere when it has regained its initial temperature. We have in this case

$$\kappa = \frac{\log p_0 - \log \Pi}{\log p_0 - \log p}.$$

In one of the experiments

$$\Pi = 1.0096, \quad p_0 = 1.0314, \quad p = 1.0155,$$

whence $\kappa = 1.3745$.

By this method M. Hirn has found 1.3845, M. Dupré 1.399, Hr. Weisbach 1.4025, M. Masson 1.419, as the value of κ for air: M. Masson found also that $\kappa = 1.30$ for carbon dioxide.

The discrepancy between these numbers is explained by the fact that the compression or expansion does not occur adiabatically as the formula implies: thus part of the heat generated by the compression is communicated to the in-rushing air and another part is lost to the walls of the vessel; and during the expansion heat is communicated by the walls to the cooled air. Hence the experiments will give better results the larger the amount of air in proportion to the surface of the vessel, that is, the larger the vessel: the stopcock too should not be opened longer than is required to equalize the internal and external pressures.

(3) But here M. Cazin¹ has pointed out another difficulty. Just as a weight depresses the pan of a spring-balance, on which it is placed, below the final position of equilibrium by reason of the velocity acquired, equilibrium being only restored after a series of oscillations, so on the opening of the stopcock more gas rushes in or out than is necessary to produce equilibrium of pressure and a series of oscillations occurs: the final pressure in the globe therefore depends on the phase of the oscillation when the stopcock is closed. M. Cazin found that by gradually increasing the time during which the stopcock was opened he obtained very fluctuating values of κ ,* tending at first to a limit from which they afterwards deviated more and more as

¹ *Ann. de ch. et de phys.* [3] lxvi. (1862) 206.

the process became less adiabatic: this limiting value is thus the nearest to the true value of κ that the experiment is capable of giving.

By connecting the globe with another vessel of the same size and containing the same gas instead of with the outer air M. Cazin was able to determine κ for different gases: he found the same value 1.41 for air, oxygen, nitrogen, hydrogen, carbon monoxide, and 1.291 for carbon dioxide.

(4) As the manometers in the above experiments were scarcely sensitive enough, Hr. Kohlrausch¹ proposed to replace them by an aneroid, which is a convenient instrument as the deviations of its needle (counted from the position in a vacuum) are proportional to the pressures, so that each division of the scale corresponds to a given change of pressure. When placed in the receiver of an air-pump the air of which was suddenly rarefied by a single stroke of the piston, an aneroid indicated that, when the time t is measured from the beginning of the stroke, the rate of change of pressure at any moment due to the heat conducted or radiated from the outside was proportional to the difference x between the actual pressure at that moment and the final pressure that ensues on the original temperature being regained, or

$$\frac{dx}{dt} = -mx,$$

whence

$$x = x_0 e^{-mt}.$$

These equations cannot be used for the period of the piston's motion, but, as the period was small, Hr. Kohlrausch assumed that the mean rate of change of pressure during the stroke was equal to the mean of the rates at the beginning and end of it: now at the beginning the rate is 0, and at the end it is $mx_0 e^{-mt_1}$, if t_1 is the length of the period, so that the variation of pressure during the stroke is $\frac{1}{2} t_1 m x_0 e^{-mt_1}$; as further the pressure at the end of the stroke is $x_0 e^{-mt_1}$ less than that finally assumed by the air, the total change of pressure during the process is $(1 + \frac{1}{2} m t_1) x_0 e^{-mt_1}$. Then if p_0 is the original pressure of the air before rarefaction, p its final pressure, and

¹ *Pogg. Ann.* cxxxvi. (1869) 618.

$p - (1 + \frac{1}{2} m t_1) x_0 e^{-m t_1} \equiv p'$ the lowest pressure caused by the rarefaction, we have

$$\kappa = \frac{\log p_0 - \log p'}{\log p_0 - \log p}$$

In Hr. Kohlrausch's experiment,

$$x_0 = 0.01522, \quad m = 0.1877, \quad t_1 = 0.75,$$

$$(1 + \frac{1}{2} m t_1) x_0 e^{-m t_1} = 0.01415, \quad p_0 = 1.00290,$$

$$p = 0.95356, \quad p' = 0.93941, \quad \text{whence } \kappa = 1.296.$$

This is not a good result, partly from the uncertainty about p' , and partly because the air was contained in a very small receiver, of capacity 6 litres only: still the method is more perfect than the former ones, as allowance is made for the heat communicated during the rarefaction.

(5) In 1870 Dr. Röntgen shewed¹ that the pressure-indications given by an ordinary aneroid are not sufficiently reliable, and, by employing instead a circular corrugated plate of German silver (as used in aneroids) let into the side of a glass globe, he obtained much better results, finding about 1.41 as the value of κ for air. In 1872 he made² a more complete series of experiments with a more perfect apparatus, consisting of a 70-litre glass globe *A* over an opening in the side of which a circular corrugated plate of German silver *B* was cemented: to

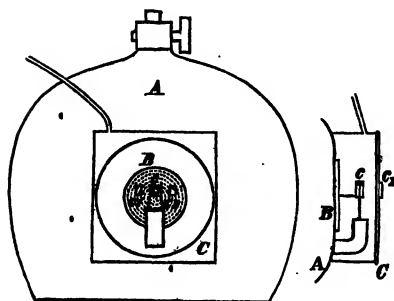


Fig. 35.

this was glued a bit of reed which was also attached to a small mirror *c* moveable about a fixed axis, so that the motion of the plate could be exactly measured by the reflexion of a distant vertical scale viewed through a telescope. This was protected from variations of atmospheric

pressure during the half-hour occupied by each experiment by an air-tight cover *C* with a plate-glass window, which

¹ *Pogg. Ann.* cxli. (1870) 552.

² *Pogg. Ann.* cxlviii. (1873) 580.

was further connected by a tube with another 70-litre globe containing air at atmospheric pressure, so that any variations of temperature during the experiment (and these were prevented as much as possible by paste-board covers and layers of hay) might have equal effects on the two sides of the plate: two small mirrors c_1, c_2 were also fixed on the outside of the window to throw comparison-reflexions of the vertical scale.

The globe A was filled by allowing the gas to be tested to stream into it for several days so that all air might be removed, and its stopcock was shut when the pressure of the gas was somewhat greater than that of the atmosphere; the stopcock was then quickly opened and shut and the maximum change of pressure (which occurs at the moment of shutting) observed; lastly, the pressure was observed when the initial temperature had been regained: then the heat communicated during the expansion (which was almost negligible except in the case of hydrogen) was allowed for by Hr. Kohlrausch's method, and κ was calculated by the ordinary formula. The means of 10 excellently agreeing experiments gave 1.4053 as the value of κ for air, 1.3052 for carbon dioxide, and 1.3852 for hydrogen: the last number is much too small, for the original temperature was regained so quickly that the change of pressure with the time could not be determined, and thus no correction applied, though much more required than in the former cases. These are the most trustworthy of the experiments yet made.

B. Newton gave the formula¹

$$v = \sqrt{\frac{e}{\rho}} \quad (11)$$

as the relation between the velocity of wave-propagation in a medium, its elasticity, and density; he considered also the temperature to remain constant, so that by (59), § 63, the elasticity is equal to the pressure: thus in air at 0°C. and under a barometric pressure of 76 c. at Paris (which is equivalent to 1013573 dynes per square centimetre), its density under these circumstances being 0.0012932 grams per c.c., the velocity of sound

¹ *Principia*, ii. § 8.

should be $\sqrt{\frac{1013573}{0.0012932}} = 27996 \text{ c. per sec.}$,—a result which is too small by over 15 per cent., the values determined by experiment ranging between 33237 (as found by MM. Bravais and Martins) and 33066 (M. Le Roux' determination). M. Laplace¹ however pointed out that the rarefactions and condensations of the air during wave-propagations cause an absorption or a production of heat, and he shewed that these constant changes of temperature in the parts of the air have the same effect as if its elasticity were increased while its temperature remained unaltered, the coefficient of increase being the ratio of the elasticity at constant entropy to the elasticity at constant volume, or κ , by (12), § 17: thus

$$v = \sqrt{\kappa \frac{e_t}{\rho}}, \quad (12)$$

whence, if v is determined by experiment, κ may be calculated.

To Professor Rankine is due the following elementary method of demonstrating this relation²—a method applicable to all waves of finite longitudinal disturbance which are of permanent type, the word *type* denoting the relation between the extent of disturbance at a given instant of the particles and their respective undisturbed positions. Let v be the linear velocity of the wave, v the specific volume of the substance which transmits the wave in its undisturbed state, m the mass that is disturbed in unit-time in a tube of unit-section (called the *mass-velocity*): then, as the wave traverses v in unit-time, the volume of substance in a tube of unit-section that is disturbed in unit-time is v , or

$$v = mv. \quad (13)$$

Consider now two imaginary planes moving with the velocity v in the direction of the wave, u_1, u_2 being the velocities of longitudinal disturbance of the particles that are, at any moment in the planes: these particles pass through them with the relative velocities $u_1 - v, u_2 - v$, and, if the specific volumes of the

¹ *Mécanique céleste*.

² *Phil. Trans.* clx. (1870) 277.

substance in its disturbed state at these planes are v_1, v_2 , the mass of substance which passes in unit-time through unit-section of each is $\frac{u_1 - v}{v_1}, \frac{u_2 - v}{v_2}$; but, as the wave is permanent, as much must leave the space between the planes as enters it, so that

$$\frac{v - u_1}{v_1} = \frac{v - u_2}{v_2} = m,$$

since these fractions must equal $\frac{v}{v}$, the velocity of the particles in the undisturbed state being zero. Thus

$$\left. \begin{aligned} u_1 &= v - mv_1, \\ u_2 &= v - mv_2, \end{aligned} \right\} \quad (14)$$

and either of these equations is the *kinematical condition of permanency*. Now the mass m having entered the space between the planes with velocity u_1 and an equal mass m having left it with the velocity u_2 , the gain of momentum $m(u_1 - u_2)$ can only be due to the difference $p_1 - p_2$ of the external pressures at the planes, as the mutual actions of the particles on each other cannot alter the momentum of the whole: thus

$$\begin{aligned} p_1 - p_2 &= m(u_1 - u_2), \\ &= m^2(v_2 - v_1) \end{aligned} \quad (15)$$

$$\text{by (14); or} \quad \frac{dp}{dv} = -m^2. \quad (16)$$

This is the *dynamical condition of permanency*: it may also be written in the form

$$p_1 + m^2 u_1 = p_2 + m^2 u_2 = p, \quad (17)$$

where p is the pressure in the undisturbed state. If ϵ represents the elasticity of the substance,

$$\epsilon = -v \frac{dp}{dv} = m^2 v = \frac{v^2}{v},$$

$$\text{or} \quad v^2 = \epsilon v = \frac{\epsilon}{\rho}, \quad (18)$$

which is Newton's formula. Now in sound-waves the compressions and rarefactions are very sudden and succeed each other exceedingly rapidly, so that the heat which is developed cannot pass from particle to particle by conduction; hence in calculating ϵ we must suppose that no heat is lost or take ϵ

as the elasticity at constant entropy, and as this is κ times the elasticity at constant temperature, or, in a perfect gas, κp , we have finally

$$v^2 = \kappa p v = \kappa \frac{p}{\rho}. \quad (19)$$

Experiment shews that there is no permanency in waves if the temperature of the medium is always the same: hence Professor Rankine points out that change of temperature and conduction of heat are necessary for permanence; but, as the transfers of heat must be from particle to particle and not from other bodies, the *thermodynamic condition for permanency* is that the total heat received by the medium is zero, or, $d\mu$ representing an element of mass,

$$\iint t d\phi d\mu = 0. \quad (20)$$

If a certain type of wave is capable of permanence, a relation must exist between the temperatures of the particles and their relative positions so that conduction may effect the proper transfers of heat. If $\frac{dt}{dx}$ is the rate of variation of temperature with the distance, and τ the conductivity, the quantity of heat received by unit-mass in the time during which the disturbance traverses it—that is, $\frac{1}{m}$ seconds—is $\frac{1}{m} d \cdot \tau \frac{dt}{dx}$; but this is also $t d\phi$, and thus

$$t d\phi = \frac{1}{m} d \cdot \tau \frac{dt}{dx},$$

whence,

$$\tau \frac{dt}{dx} = a + m f t d\phi,$$

and

$$x = b + \int \frac{\tau dt}{a + m f t d\phi}. \quad (21)$$

These formulae are general: they cannot in general be evaluated except for perfect gases.

(1) The velocity of sound has been determined by direct experiment. In air at 0°C . MM. Bravais and Martins found 33237, Hrn. Moll, van Beek, and Kuytenbrouwer 33226, the French Academy 33200 in 1738 and 33120 in 1822, M. Regnault 33070, M. Le Roux 33066.

(2) This velocity has also been determined indirectly. If λ is the wave-length of a particular note and n its frequency of vibration, then $v = n\lambda$: thus a note may be produced by an organ-pipe, and n measured by a siren, λ being

$$\frac{2(l + r + g)}{\pi} \quad \text{or} \quad \frac{4(l + r)}{2\pi - 1},$$

according as the pipe is open or stopped, l being its length, x the correction for the mouth-piece, y the correction for the open end, n the number of the note in the series of tones which the pipe can sound.

For the velocity of sound in air at 0°C . M. Dulong has by this method found 33300, Hr. Seebeck 33277, M. Schneebeli 33206, Hr. Wertheim 33133.

(3) Hr. Kayser has lately experimented on the velocity of sound by means of Professor Kundt's dust-figures, which give very exactly the wave-length λ corresponding to a given tone of vibration-frequency n , and he thus finds 33250 as the value of v at 0°C . for air.

We may hence take 33200 as not very far from the true value of v for air, and in this case

$$\sqrt{\kappa} = \frac{33200}{27996} \text{ or } \kappa = 1.4063.$$

As a final result then we shall take the mean between this number and that determined by Dr. Röntgen, or 1.4058, as the value of κ for air, and thus $k = \frac{9.9263}{1.4058} = 7.0610$. We

have throughout the calculations considered air a perfect gas, but the error we have introduced thereby cannot be very great; and if we proceed to find the value of γ on this supposition by (52), § 63, we obtain a result almost identical with Dr. Joule's; thus

$$\gamma = \frac{\kappa}{\kappa - 1} \frac{R}{C} = \frac{1.4058}{0.4058} \times \frac{2.8725}{0.2389} = 41.65.$$

A very small error in the value of κ would cause a large one in γ , since

$$\delta\gamma = -\frac{\delta\kappa}{(\kappa-1)^2} \frac{R}{C} = -\gamma \frac{\delta\kappa}{\kappa(\kappa-1)} = -73\delta\kappa,$$

on substituting 41.55 for γ and 1.4058 for κ .

APPLICATION TO SOLIDS AND LIQUIDS.

75. Our experimental data are much fewer and much more uncertain for solid and liquid bodies than for gases: yet such as they are they shew a very fair agreement with the theory.

The best-known quantity for such substances is the *real coefficient of expansion under constant pressure*, when the pressure is one atmosphere: it is denoted by α , and, as it changes very little with the pressure, we may consider it a function of the temperature and write

$$\frac{\partial v}{\partial t} = \alpha v. \quad (22)$$

Other experiments give the volume-elasticity at constant temperature, or its reciprocal the *true coefficient of compressibility at constant temperature* which is denoted by β , so that

$$\frac{\partial v}{\partial p} = -\beta v. \quad (23)$$

The variation of β with the pressure is not known but seems to be negligible: its variation with the temperature is not slight, so that it must be considered a function of t .

These two results give us the variation of the pressure with the temperature when the volume remains unchanged; for

$$\frac{\partial p}{\partial t} \equiv -\frac{\frac{\partial v}{\partial t}}{\frac{\partial v}{\partial p}} = \frac{\alpha}{\beta}. \quad (24)$$

The equations of §§ 16, 53, 54 therefore become

$$\left. \begin{aligned} K - k &\equiv t \frac{\partial p}{\partial t} \frac{\partial v}{\partial t} = \frac{\alpha^2}{\beta} vt, \\ l &\equiv t \frac{\partial p}{\partial t} = \frac{\alpha}{\beta} t, & L &\equiv -t \frac{\partial v}{\partial t} = -\alpha vt, \\ p &\equiv k \frac{\partial t}{\partial p} = K \frac{\beta}{\alpha} - \alpha vt, & v &\equiv K \frac{\partial t}{\partial v} = \frac{K}{\alpha v}. \end{aligned} \right\} \quad (25)$$

76. Application to water. M. Rossetti discussed¹ in 1868 the results of the best experiments on the density of water between 0° and 100°C ., and compared them with an elaborate series of observations made by himself with a dilatometer: he concluded that the specific volume of water between these temperatures is best represented by the formula

$$v = 1 + a_1(\theta - 4)^2 - b_1(\theta - 4)^{3.5} + c_1(\theta - 4)^3,$$

¹ *Ann. de ch. et de phys.* [4] x. (1867) 461, xvii. (1869) 370.

where

$a_1 = 8.37991 \times 10^{-6}$, $b_1 = 3.78702 \times 10^{-7}$, $c_1 = 2.24329 \times 10^{-8}$,
 θ representing $t - 273.7$ or centigrade temperature; hence

$$\frac{\partial v}{\partial t} = 2a_1(\theta - 4) - 2.6b_1(\theta - 4)^{1.6} + 3c_1(\theta - 4)^3.$$

The indices 1.6 and 2.6 must be considered odd and even respectively.

For temperatures between 100° and 182°C . with a pressure of about 15 atmospheres M. Hirn gives the formula¹

$$v = 1 + a_2\theta + b_2\theta^2 + c_2\theta^3 - d_2\theta^4,$$

where $a_2 = 1.08679 \times 10^{-4}$, $b_2 = 3.00737 \times 10^{-6}$,
 $c_2 = 2.87304 \times 10^{-9}$, $d_2 = 6.64570 \times 10^{-13}$;

and
$$\frac{\partial v}{\partial t} = a_2 + 2b_2\theta + 3c_2\theta^2 - 4d_2\theta^3.$$

His apparatus consisted of a copper vase *A* communicating by a vertical pipe *B* with a cast-iron vessel *C*, from which an iron tube *D* was led $10\frac{1}{2}$ metres vertically upwards, its upper part terminating in a wide glass tube *E*, graduated in c.c., and with a short branch-pipe *F*: water filled the vase *A* and the upper part of *B*, the rest of the apparatus being filled with mercury up to *E*. *A* was heated by two gas-burners enclosed with it in the double cover *G*, whose inner walls were of tinned iron and the outer of wood: the water was continuously agitated by the stirrer *H*, the axis of which passed through *B* and *C* so as to be worked from outside, and the expansion was measured by the mercury that overflowed into *E* or was drawn off at *F*.

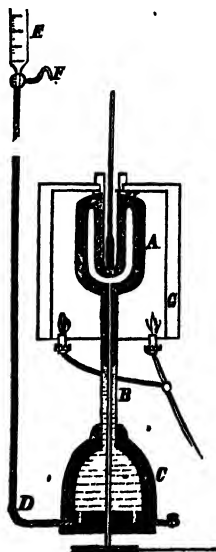


Fig. 36.

The best experiments on the compressibility of water are those of M. Grassi: from his first series² Professor

¹ *Ann. de ch. et de phys.* [4] x. (1867), 32.

² *C. R.* xxvii. (1848) 153.

Rankine shewed¹ that the compressibility is inversely proportional to the density and absolute temperature jointly, but the second and more complete series² gives no countenance to this law. If the results of this latter series are plotted on a diagram, they are found to disagree very considerably: we may however deduce from them the formula

$$\beta = a_3 + b_3 \theta + c_3 \theta^2,$$

where

$a_3 = 5.0357 \times 10^{-8}$, $b_3 = 2.8922 \times 10^{-7}$, $c_3 = 3.0743 \times 10^{-9}$, pressure being measured in c. g. s. atmospheres. The range of the experiments was between 0° and 53°C .

We get also from M. Bosscha's calculation of M. Regnault's experiments

$$\begin{aligned} K &= 41.55 (1 + 0.00022 \theta) \\ &= a_4 + b_4 \theta, \end{aligned}$$

where

$$a_4 = 41.55, \quad b_4 = 9.141 \times 10^{-3}.$$

In these experiments a mass m_3 of water at θ_3 was forced by its steam pressure from the boiler to the calorimeter, raising the mass m_1 of water contained therein from θ_1 to θ_2 , but the kinetic energy thus converted into heat was not taken into account. If F is the pressure of saturated steam at θ_3 , Π the atmospheric pressure, v_3 the specific volume of water at θ_3 , $K_{1,2}$ the mean specific heat of water between θ_1 and θ_2 , $K_{2,3}$ the mean specific heat between θ_2 and θ_3 , then

$$m_1 K_{1,2} (\theta_2 - \theta_1) = m_3 K_{2,3} (\theta_3 - \theta_2) + m_3 v_3 (F - \Pi);$$

and it is the last term that M. Regnault neglected. Professor Rankine applied the necessary correction and proposed the formula³

$$K = K_4 \{1 + 0.000001 (\theta - 4)^2\};$$

but this does not represent so well the specific heats at low temperatures, while at high temperatures it differs very slightly from Hr. Bosscha's, which we therefore prefer.

From these data we have made the following tables, which will give an idea of the magnitudes of the quantities in question.

¹ *Proc. R. S. E.* iii. (1851) 58, or *Phil. Mag.* [4] i. (1851) 548.

² *Ann. de ch. et de phys.* [3] xxxi. (1851) 477.

³ *Trans. R. S. E.* xx. (1851) 441.

θ	v	$\frac{\partial v}{\partial t}$	α	β	$\frac{\partial v}{\partial p}$	$\frac{\partial p}{\partial t}$
0	1.000119	-0.0000569	-0.0000569	+0.0000504	-0.0000504	-1.130
25	1.002866	+0.0002532	+0.0002530	+0.0000450	-0.0000451	+5.616
50	1.011945	+0.0004629	+0.0004574	+0.0000436	-0.0000441	+10.496

θ	K	k	κ	l	L	p	y
0	41.550	41.532	1.0004	-309.2	+0.0156	-36.761	-730228
25	41.778	41.353	1.0103	+1677.6	-0.0756	+7.356	+164660
50	42.007	40.434	1.0389	+3397.5	-0.1498	+3.854	+90754

We should notice that k decreases, while K and κ increase, as the temperature rises.

77. Application to other substances. We will consider ether and alcohol as M. Grassi has experimented on them: Hr. Kopp's researches on their dilatation lead to the formulæ

$$v = v_0(1 + a\theta + b\theta^2 + c\theta^3),$$

$$\frac{\partial v}{\partial t} = v_0(a + 2b\theta + 3c\theta^2),$$

wherein the values of the constants are

$$\text{for ether} \quad v_0 = \frac{1}{0.73658},$$

$$a = 1.48026 \times 10^{-3}, \quad b = 3.50316 \times 10^{-8}, \quad c = 2.7007 \times 10^{-8};$$

$$\text{for alcohol} \quad v_0 = \frac{1}{0.80950},$$

$$a = 1.04139 \times 10^{-3}, \quad b = 7.836 \times 10^{-7}, \quad c = 1.7618 \times 10^{-8}.$$

M. Regnault's experiments also give

$$\begin{aligned} \text{for ether} \quad K &= 41.55(0.52901 + 0.0005916\theta) \\ &= 21.980 + 0.02458\theta, \end{aligned}$$

for alcohol

$$\begin{aligned} K &= 41.55(0.54754 + 0.0022436\theta + 0.000006618\theta^2) \\ &= 22.751 + 0.09322\theta + 0.000275\theta^2. \end{aligned}$$

We hence deduce for the temperatures of M. Grassi's experiments :—

Fluid	θ	$\frac{\partial v}{\partial t}$	β	$\frac{\partial v}{\partial p}$	$\frac{\partial p}{\partial t}$	K	k	κ
Ether	0	0.002010	0.0001095	-0.0001487	13.517	21.980	14.545	1.5112
"	14	0.002164	0.0001381	-0.0001915	11.299	22.324	15.288	1.4602
Alcohol	7.3	0.001304	0.0000817	-0.0001017	12.825	23.445	18.746	1.2507
"	13.1	0.001323	0.0000892	-0.0001117	11.845	24.019	19.525	1.2302

In both these cases we see that k increases (and K also), while κ decreases, as the temperature rises—the reverse action to what occurs in water.

As a type of solid bodies we may consider silver. Dr. Matthiessen finds for its linear expansion the formula

$$l = l_0(1 + a\theta + b\theta^2),$$

where $a = 1.809 \times 10^{-5}$, $b = 1.35 \times 10^{-8}$;

hence $v = v_0(1 + a\theta + b\theta^2)^3$,

$$a = \frac{3(a + 2b\theta)}{1 + a\theta + b\theta^2}.$$

Now Hr. Wertheim found 1.4004×10^{-4} for the linear compressibility of silver at low temperatures with the weight of a kilogram and the millimetre as units, or

$$\frac{1.4004 \times 10^{-4}}{0.9809 \times 10^2} = 1.4277 \times 10^{-6}$$

in c. g. s. units (since the weight of a kilogram at Paris is 0.9809 megadynes), and he has shewn further that the cubical compressibility of metals is sensibly equal to their linear compressibility: we have therefore $\beta = 1.4277 \times 10^{-6}$. Calculating

for the temperature 0°C . where $v_0 = \frac{1}{10.551}$, we find

$$a = 5.427 \times 10^{-5}$$

and $K - k = \frac{(5.427 \times 10^{-5})^2 \times 273.7}{(1.4277 \times 10^{-6}) \times 10.551} = 0.0534$;

but $K = 41.55 \times 0.0559 = 2.3226$, and thus $k = 2.2692$ and $\kappa = 1.0235$. By an entirely different method Hr. Edlund¹ has found $\kappa = 1.0203$.

78. Adiabatic compression. When bodies are compressed without losing or gaining any heat, there subsists the relation

$$K dt + L dp = 0$$

or
$$\left(\frac{\partial p}{\partial t}\right)_\phi = -\frac{K}{L} = \frac{K}{avt};$$

hence the small increase of temperature ϑ due to an increase of pressure ω when no heat is gained or lost is very approximately given by

$$\vartheta = \frac{at}{K\rho} \omega, \quad (26)$$

if ρ is the density of the substance. This formula is due² to Sir W. Thomson, who also earlier gave the formula³

$$\left. \begin{aligned} \vartheta &= -\frac{at}{K\beta - a^2vt} v \\ &= -\frac{at}{k\beta} v \end{aligned} \right\} \quad (27)$$

approximately, for the small increase of temperature ϑ that occurs on a slight adiabatic expansion v , as may be found by a method similar to that above.

Dr. Joule has verified⁴ the former formula by compressing water in a copper vessel connected with a cylinder on the piston of which weights could be placed, a copper-iron thermoelectric junction (which was found to be uninfluenced in action by the pressures to which it was subjected) being placed in the centre of the vessel to measure the thermal effect: each experiment lasted 40" (the time required by the galvanometer-needle to assume a new position), and it was found that in this short time the cooling due to the expansion of the vessel did not affect the thermopile. The experimental results were:—

¹ *Pogg. Ann.* cxxvi. (1865) 566.

² *Proc. R. S.* viii. (1857) 568, or *Phil. Mag.* [4] xv. (1858) 541.

³ *Trans. R. S. E.* xx. (1851) 283, or *Phil. Mag.* [4] iv. (1852) 171.

⁴ *Phil. Trans.* cxlix. (1859) 133.

θ	α	β	
		observed	calculated
1.2	25.690	-0.0083	-0.0070
5.	25.690	+0.0044	+0.0027
11.69	25.690	+0.0205	+0.0189
18.38	25.690	+0.0314	+0.0333
30.	25.690	+0.0544	+0.0563
31.37	15.856	+0.0394	+0.0362
40.4	15.856	+0.0450	+0.0465

The experiments were repeated on oil with similarly satisfactory results.

We can easily prove as above the formula

$$\left(\frac{\partial p}{\partial v}\right)_\phi = -\frac{\kappa\rho}{\beta},$$

or it may be deduced from (26) and (27) together. This differential coefficient is the tangent of the inclination of the adiabatic to the v -axis, and thus for the same density the adiabatic is the steeper, the greater $\frac{\kappa}{\beta}$. Now for water κ increases and β diminishes as the temperature rises, and thus for the same density the adiabatics are the steeper, the higher the temperature: hence in Fig. 18, § 44, the adiabatic (2) corresponds to the higher temperature. M. Grassi's actual determination of β seems to indicate that it has a maximum value at 1.5°C. , and in this case the above conclusion holds only over 1.5°C. : the determinations are however far too uncertain and irregular either to prove that there is a maximum or to shew the temperature at which it occurs.

79. Thermal effects accompanying traction. If we submit a solid rod, of indeterminate section and subject to a lateral pressure which is constant, to the action of a longitudinal stress in the direction of its length, so as to cause its elongation or contraction, we shall produce thermal phenomena similar

to the above. If T be the stress acting as a tension, x the length of unit-mass of the rod, K' its specific heat under constant tension, L' the latent heat for an increase of tension at constant temperature, then

$$dE - T dx = dH = K' dt + L' dT,$$

the negative sign being used in the first expression as during elongation work is done *by* the tension *on* the body: hence we find exactly as in §§ 52, 53,

$$\left. \begin{aligned} L' &= t \frac{\partial x}{\partial t} \\ &= t \alpha' x, \end{aligned} \right\} \quad (28)$$

if α' is the real coefficient of linear expansion under longitudinal stress. We may also shew this by considering unit-mass of the rod to perform a Carnot's cycle $ABCD$ by undergoing (1) a diminution of tension without loss or gain of heat till the temperature falls by δt , (2) an increase of tension δT , the temperature being kept constant by the addition of heat $L' \delta T$, (3) a further increase of tension without loss or gain of heat till the initial temperature is attained, (4) a diminution of the tension to its initial value, the temperature being maintained constant by the withdrawal of heat: then by Carnot's principle,

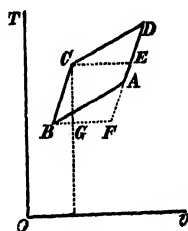


Fig. 37.

$$\frac{\text{area } ABCDA}{L' \delta T} = \frac{\delta t}{t}.$$

Now the area $ABCD$ may be considered a parallelogram and therefore equal to the area $BCEFB$ or $CE \times GC$; but CE is the elongation due to the change of temperature δt under constant tension or $\frac{\partial x}{\partial t} \delta t$, and GC is the change of tension δT ; hence

$$\frac{\frac{\partial x}{\partial t} \delta t \delta T}{L' \delta T} = \frac{\delta t}{t},$$

whence equation (28).

If, therefore, the rod is suddenly stretched without gaining or losing heat, we have $(\frac{\partial t}{\partial T})_{\phi} = -\frac{L'}{K'} = -\frac{\alpha' x t}{K'}$;

or the small change of temperature \mathfrak{S} due to an increase of tension \mathfrak{U} adiabatically is $\mathfrak{S} = -\frac{\alpha' x t}{K'} \mathfrak{U}$. (29)

The negative* sign indicates a cooling on extension in those bodies which expand when heated, and similarly a heating on extension in those bodies which contract as their temperature rises. No experiments have been made to determine K' , the specific heat under a constant longitudinal tension, but in calculations it is assumed equal to K , the specific heat under a constant hydrostatical pressure, from which it cannot very much differ: similarly, as the dependence of α' , the coefficient of linear expansion under longitudinal stress, upon the stress has not been experimentally determined, it is generally assumed equal to the real coefficient of linear expansion under ordinary atmospheric pressure.

Dr. Joule has verified¹ this formula also by experimenting on cylindrical bars about 30·48 c. long and 0·635 c. in diameter, the upper ends of which were screwed into a fixed piece of metal and the lower ends attached to a lever on whose extremity weights could be hung without the operator approaching the apparatus. The change of temperature was measured by a thermo-electric junction of fine copper and iron wires inserted into a hole, 0·063 c. in diameter, bored through the centre of the bar. He obtained the following:—

	θ	κ	α'	K'	\mathfrak{U}	\mathfrak{S}	
						calculated	observed
Iron	13·3	0·4285	$1·2204 \times 10^{-5}$	4·728	321·2	-0·1020	-0·1007
Hard steel	1·7	0·4483	$1·3620 \times$ „	4·255	321·2	-0·1270	-0·1620
Cast iron	9·3	0·5246	$1·1250 \times$ „	4·978	324·9	-0·1090	-0·1481
Copper	1·2	0·3773	$1·7182 \times$ „	3·953	317·7	-0·1399	-0·1740
Lead	4·8	0·0746	$2·8575 \times$ „	1·305	80·0	-0·0364	-0·0531

¹ *Phil. Trans.* cxlix. (1859) 98.

Similarly satisfactory results were obtained with gutta-percha and different kinds of wood, and also when the rods were compressed instead of being elongated.

The behaviour of india-rubber, the peculiarities of which were first pointed out by Mr. Gough¹, was also carefully examined. When suddenly stretched it undergoes a heating instead of a cooling effect, and is immediately cooled if allowed to contract: Sir W. Thomson therefore concluded that α' is negative, or that a stretched piece of india-rubber will contract when its temperature is raised—a fact demonstrated by Dr. Joule, who found that when initially stretched to double its length it contracts by $\frac{1}{10}$ th of that length on rising through 50 degrees. The elasticity of india-rubber is very imperfect and at low temperatures it becomes rigid: it then acts like a metal, being cooled on extension and warmed on compression. Better experiments can be made with vulcanized india-rubber, the elasticity of which is more permanent, and the general facts observed are—(1) the effects of adding or removing tension are sensibly equal but opposite, (2) when the tension is small but continuously increased, there is at first a cooling effect which reaches a maximum and ultimately becomes a heating effect that increases more rapidly than the tension.

Hr. Schmulewitsch² has also shewn that the effect of heating a stretched piece of india-rubber is to lengthen it if the tension is small, and to shorten it if the tension is large: thus for a certain tension there will be neither elongation nor contraction. He determined this tension and the corresponding elongation in the following cases:—

	length	diameter	breadth	thickness	tension	elongation
Tube	10.3	0.55		0.1	0.1746	0.097
Rod	8.25	0.7			0.2942	0.102
Band	10.3		0.9		0.0392	0.129

¹ *Mem. Literary and Philosophical Society of Manchester*, [2] i. (1805) 288.

² *Vierteljahrsschrift der Naturforsch. Gesellschaft, Zürich*, xi. 202.

This example shews that the values of α' should in all cases be determined by special experiment, for the vulcanized india-rubber used by Dr. Joule *dilated* when heated in an unstretched condition, its coefficient of cubical expansion 5.26×10^{-4} being greater than that of any other solid.

Hr. Edlund¹ has made similar experiments on wires: these

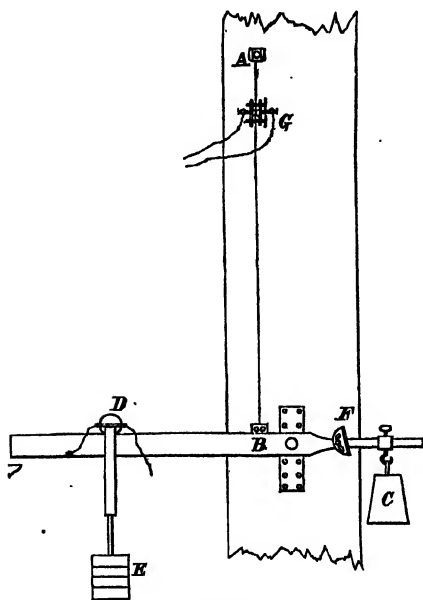


Fig. 38.

were fixed by their upper end *A*, the lower end being so fastened to a moveable lever at *B* as to be instantly loosened on a pin being drawn. On the lever, the weight of which was counterpoised by *C*, was a roller *D* that supported a weight *E* which could thus easily be moved backwards and forwards, and the elongation of the wire caused thereby was estimated from the angular displacement of the lever determined by means

of the mirror *F*. The temperature of the wire was determined by a small thermo-electric element *G* consisting of a crystal of antimony and another of bismuth separated by the wire against which they were pressed by springs. An experiment included three processes: (1) the weight *E* was rapidly pulled to the far end of the lever and the thermal effect θ_1 , which was always a cooling, observed; (2) on the wire regaining its initial temperature (known by the return of the galvanometer needle

¹ *Pogg. Ann.* cxiv. (1861) i, cxxvi. (1865) 539.

to its initial position) the weight E was pulled back to its first position, and the thermal effect \mathfrak{S}_2 , a warming, determined; (3) when the weight was at the far end of the lever, the pin was suddenly withdrawn and the wire loosened; its contraction was unaccompanied by external work and caused the thermal effect \mathfrak{S}_3 . With a steel pianoforte wire, 59 c. long and 0.114 c. in diameter; the following results were obtained:—

\mathfrak{T}	\mathfrak{S}_1	\mathfrak{S}_2	\mathfrak{S}_3	$\mathfrak{S} = \frac{\mathfrak{S}_2 - \mathfrak{S}_1}{2}$	$\frac{\mathfrak{S}}{\mathfrak{T}}$	$\frac{\mathfrak{S}_3 - \mathfrak{S}}{\mathfrak{T}^2}$
2.778	-0.911	+0.843	+1.294	0.877	0.316	0.0540
3.499	-1.054	+1.033	+1.695	1.044	0.298	0.0532
4.270	-1.312	+1.312	+2.301	1.312	0.307	0.0542
4.939	-1.446	+1.431	+3.001	1.438	0.290	0.0641
5.319	-1.742	+1.701	+3.608	1.722	0.324	0.0530

We thus see that (1) the values of \mathfrak{S}_1 and \mathfrak{S}_2 are equal but opposite (their means being in the fifth column), and they correspond to equal but opposite changes of length; (2) they are proportional to the tension \mathfrak{T} (the mean coefficient of proportion being 0.307) and thus to the change of length λ ; (3) when external work is done the heating \mathfrak{S} is less than the heating \mathfrak{S}_3 that accompanies free contraction; (4) the difference $\mathfrak{S}_3 - \mathfrak{S}$ is proportional to the square of the tension (the mean coefficient of proportion being 0.536 if experiment 4, in which \mathfrak{S}_3 must be wrong, is omitted) and thus to the product of the tension and contraction or to the external work done, as we should expect. From the uncertainty as to the values of α' and K' the formula (29) could not be verified.

80. Thermal effect of drawing out a film of liquid.

Sir W. Thomson has applied Carnot's principle to the interesting case of a soap-bubble or other liquid film¹. If T_1, T_2 are the tensions in the directions of principal curvature of one side of the film, and r_1, r_2 the radii of principal curvature, then

¹ *Proc. R. S.* ix. (1858) 255.

the corresponding pressure is $\frac{T_1}{r_1} + \frac{T_2}{r_2}$, or $\frac{2T}{r}$ when the surface is spherical, so that $T_1 = T_2 = T$ and $r_1 = r_2 = r$. In the case of a thin spherical soap-bubble, the values of T and r may be supposed the same on each side of the film, and hence the inside pressure will be $\frac{4T}{r} + \Pi$, when Π is the atmospheric pressure. Then the work done per unit of augmentation of the area of one side of the film will be $2T$.

Now for a given liquid T varies, and in general decreases, as the temperature rises, as is shewn by the different heights to which the liquid rises in a capillary tube at different temperatures, the heights being in general the less the higher the temperatures. Thus T, T' being the tensions at the temperatures t, t' , the work $2(T - T')$ will be gained if a bubble on the end of a tube is allowed to collapse so as to lose unit-area at t , and then, after being heated to t' , is blown up again to its original dimensions; or, if the difference of temperature is small and equal to δt , there will be an absorption of heat H at the higher temperature and at the lower an evolution of heat which is infinitesimally less by $-2 \frac{dT}{dt} \delta t$, the work done, whence by Carnot's principle

$$\frac{-2 \frac{dT}{dt} \delta t}{H} = \frac{\delta t}{t},$$

or
$$H = -2t \frac{dT}{dt}$$

'Hence if a film such as a soap-bubble be enlarged, its area being augmented in the ratio of 1 to m , it experiences a cooling effect to an amount calculable by finding the lowering of temperature produced by removing a quantity of heat equal to $-mt \frac{dT}{dt}$ from an equal mass of liquid unchanged in form.'

For water $T = 81$ dynes per centimetre at 20°C. , or the work per square centimetre in drawing out a film = 162 ergs; also $\frac{dT}{dt} = -\frac{T}{550}$ about.

Hence at 20° c., where $t = 293.7$, the heat that must be removed to produce the cooling effect per square centimetre of surface-extension is 86.5 ergs. Thus if a gram of water be drawn out to a film of 100 square centimetres, the cooling effect will be $100 \times \frac{86.5}{41.55 \times 10^6} = \frac{1}{4803}$ degree c., and the work spent in drawing it out is $100 \times 162 = 16200$ ergs, and is equivalent to a heating effect of $\frac{16200}{41.55 \times 10^6} = \frac{1}{2565}$ degree c.; hence the total energy of the water is as much increased when it is drawn out to 100 square centimetres at its original temperature as if it were raised through

$$\frac{1}{4803} + \frac{1}{2565} = \frac{1}{1672} \text{ degree c.,}$$

or its energy is increased by 1 megalerg when it is drawn out to 4036 sq. c.

CHAPTER VIII.

Change of State.

§1. Apparent discontinuity. Under certain circumstances we find that heat given to a body at constant pressure does not increase its temperature as in the general case, but produces molecular changes, altering its state from the solid to the liquid form, from the liquid to the gaseous, or from the solid to the gaseous: these are the processes of fusion, vaporization, and sublimation. When a higher form exists simultaneously and in contact with a lower form of the same body, it is said to be *saturated*; and for this case the general thermodynamic equations require modification.

Denoting by f (the letter generally used to express vapour pressures) the pressure of a body in a saturated condition, by s', s the specific volumes (*i.e.* the volumes of unit-mass) of the body in the higher and lower form, these quantities being functions of t , and by m the proportion of the substance in the higher form in unit-mass of the mixture, we have by § 12

$$\begin{aligned} v &= (s' - s)m + s \\ &= mu + s, \end{aligned} \tag{1}$$

if we write u for $s' - s$, so that u is a function of t : also

$$f = F(t).$$

The form of the function $F(t)$ has been found by Professor Rankine¹ on a certain hypothesis as to the molecular constitution of bodies to be

$$\log f = a - \frac{b}{t} - \frac{c}{t^2} - \dots, \tag{2}$$

t denoting absolute temperature, and $a, b, c \dots$ being constant

¹ *Edin. New Phil. Journ.* xlvii. (1849) 28.

for a given substance. The hypothesis referred to is that 'the pressure of a vapour in presence of its liquid or solid is the result of an expansive elasticity in the vapour balanced by an attractive force tending to condense it on the liquid or solid surface.'

The heat absorbed by unit-mass in changing state is called the *latent heat*: it is a function of the temperature, and will be denoted by λ megalergs. Now the total volume is increased during this change of state by $s' - s$ or u under the constant pressure f , so that external work fu is done in addition to the work against molecular forces: hence the heat λ' really concerned in the molecular change is given by

$$\lambda' = \lambda - fu. \quad (3)$$

82. General equation. Let s', s be the specific heats of a body in the higher and lower form respectively when saturated, that is, the heat requisite to raise the temperature by one degree when the pressure varies so that equation (2) is always satisfied: these quantities are functions of t , and as the temperature and pressure alter simultaneously we have

$$s = K + L \frac{df}{dt}, \quad s' = K' + L' \frac{df}{dt}, \quad (4)$$

K, L having the ordinary meanings and referring to the lower form of the body, K', L' referring to the higher.

When a saturated mixture takes in heat in the general case, the temperature of the whole is raised and a portion of the lower form is transformed into the higher; thus addition of heat dH will raise the temperature by dt , the lower form taking $(1-m)s dt$ and the higher $ms' dt$, and cause dm to change state and render latent λdm : hence

$$dH = \{(s' - s)m + s\} dt + \lambda dm. \quad (5)$$

83. Application of the First Law. Since

$$dH = dE + f dv,$$

$$dE = \left\{ (s' - s)m + s - f \frac{\partial v}{\partial t} \right\} dt + \left(\lambda - f \frac{\partial v}{\partial m} \right) dm:$$

but this is a perfect differential; hence

$$\frac{\partial}{\partial m} \left\{ (s' - s)m + s - f \frac{\partial v}{\partial t} \right\} = \frac{\partial}{\partial t} \left(\lambda - f \frac{\partial v}{\partial m} \right),$$

$$\text{or} \quad \frac{d\lambda}{dt} + s - s' = \frac{df}{dt} \frac{\partial v}{\partial m} = \varpi u, \quad (6)$$

by (1), on writing, as is very convenient, ϖ for $\frac{df}{dt}$. This relation was first given by Professor Clausius¹, but by a somewhat cumbrous method; the above exact demonstration is due to Sir W. Thomson².

§4. Application of the Second Law. Since $\frac{dH}{t}$ is a perfect differential,

$$\frac{\partial}{\partial m} \cdot \frac{(s' - s)m + s}{t} = \frac{\partial}{\partial t} \cdot \frac{\lambda}{t}, \quad (7)$$

$$\text{or} \quad \frac{d\lambda}{dt} + s - s' = \frac{\lambda}{t}. \quad (8)$$

$$\text{Hence by (6),} \quad \lambda = \varpi u t. \quad (9)$$

Equation (8) was first given by Hr. Clausius in the paper demonstrating (6). Equation (9) may be obtained by the direct application of Carnot's principle: for when δm changes state at constant temperature, heat $\lambda \delta m$ is absorbed and the volume is increased by $u \delta m$; thus, the change of pressure in the small cycle being $\frac{df}{dt} \delta t$, we have

$$\frac{u \delta m \cdot \frac{df}{dt} \delta t}{\lambda \delta m} = \frac{\delta t}{t},$$

whence the above relation. It was thus first found by Sir W. Thomson³, who used a different notation and denoted Carnot's Function by the general symbol μ instead of $\frac{1}{t}$ as later assumed: Professor James Thomson⁴ at the same time virtually gave it from consideration of the circumstances attending the fusion of ice as detailed in § 89.

¹ *Pogg. Ann.* lxxix. (1850) 389, trans. *Phil. Mag.* [4] ii. (1851) 16.

² *Trans. R. S. E.* xx. (1851) 285, or *Phil. Mag.* [4] iv. (1852) 174.

³ *Trans. R. S. E.* xvi. (1849) 556, equation (6).

⁴ *Trans. R. S. E.* xvi. (1849) 575.

Relation (9) shews that ϖ is positive or negative according as s' is greater or less than s : thus according as a body expands or contracts in changing state from a lower to a higher form, so does an increase of pressure on the body in a saturated state raise or lower its temperature. This result might have been expected: if fusion, for instance, is accompanied by increase of volume, that is, by further separation of the molecules, compression must reconvert some of the liquid into the solid form, and by rendering sensible the corresponding latent heat must increase the temperature of the whole; and *vice versa*, if fusion diminishes the bulk of a body, compression will liquefy part of the solid and the necessary absorption of heat will diminish the temperature of the whole.

This relation also gives the specific volume in the form

$$v = s + \frac{m\lambda}{\varpi t}. \quad (10)$$

85. Determination of the Entropy. From (7) we have

$$s' - s = t \frac{d}{dt} \cdot \frac{\lambda}{t}; \quad (11)$$

hence the general equation (5) may be written

$$\begin{aligned} dH &= s dt + t \left\{ m \frac{d}{dt} \cdot \frac{\lambda}{t} dt + \frac{\lambda}{t} dm \right\} \\ &= s dt + t d \cdot \frac{m\lambda}{t}, \end{aligned} \quad (12)$$

a very convenient form. The entropy is therefore given by

$$\begin{aligned} \frac{dH}{t} &= d \cdot \frac{m\lambda}{t} + \frac{s}{t} dt, \\ \text{whence} \quad \phi - \phi_0 &= \frac{m\lambda}{t} - \frac{m_0 \lambda_0}{t_0} + \int_{t_0}^t \frac{s}{t} dt. \end{aligned} \quad (13)$$

86. Determination of the Intrinsic Energy. From (5), (6), (1), and (10),

$$\begin{aligned} dE &= s dt + \lambda dm + (s' - s) m dt - f dv \\ &= s dt + \lambda dm + \left(m \frac{d\lambda}{dt} dt - m u \frac{df}{dt} dt \right) - f d \cdot (mu + s) \end{aligned}$$

$$\begin{aligned}
 &= (s - f \frac{ds}{dt}) dt + d \cdot m (\lambda - fu), \\
 &= (s - f \frac{ds}{dt}) dt + d \cdot (v - s) (\varpi t - f).
 \end{aligned}$$

Hence by integration,

$$E - E_0 = m (\lambda - fu) - m_0 (\lambda_0 - f_0 u_0) + \int_{t_0}^t (s - f \frac{ds}{dt}) dt, \quad (14)$$

$$= (v - s) (\varpi t - f) - (v_0 - s_0) (\varpi_0 t_0 - f_0) + \int_{t_0}^t (s - f \frac{ds}{dt}) dt. \quad (15)$$

These equations and that of the preceding article may easily be deduced from the general relations (49), § 61.

87. Latent heat. The integration of (11) determines

$$\frac{\lambda}{t} = \frac{\lambda_0}{t_0} + \int_{t_0}^t \frac{s' - s}{t} dt. \quad (16)$$

We may also express the real internal work λ' as

$$\lambda' = u (\varpi t - f) = u t^2 \frac{d}{dt} \cdot \frac{f}{t}, \quad (17)$$

by (3) and (9). Thus λ' is zero when $\frac{d}{dt} \log_e f = \frac{1}{t}$.

88. Expansion along an Adiabatic. In this case there is no change of entropy, and equation (13) therefore gives

$$\frac{m\lambda}{t} - \frac{m_0\lambda_0}{t_0} + \int_{t_0}^t \frac{s}{t} dt = 0, \quad (18)$$

whence m can be determined for any period of the process. We have here assumed not only that there is neither gain nor loss of heat, but also that no kinetic energy is acquired or communicated: this supposition requires the external pressure to vary with and be always equal to that of the mixture.

The work done during a finite change of volume is shewn by § 32 to be the right-hand expression of (14) or (15) with every sign changed.

From (10) and (18),

$$v = s + \frac{1}{\varpi} \left(\frac{m_0\lambda_0}{t_0} - \int_{t_0}^t \frac{s}{t} dt \right);$$

and according as $(\frac{\partial v}{\partial t})_\phi$ (which is found by differentiating this

expression with respect to t) is positive or negative will compress lower or raise the temperature. It is necessarily negative when both ϖ and $\frac{s}{t}$ increase with t .

On differentiating (18) we obtain

$$\left(\frac{\partial m}{\partial t}\right)_\phi = -\frac{1}{\lambda} \left\{ s + m t \frac{d}{dt} \cdot \frac{\lambda}{t} \right\} \\ = -\frac{1}{\lambda} \{ s + m (s' - s) \},$$

which we might get at once from (5); hence according as the expressions within the brackets are positive or negative will an increase of temperature diminish or increase the value of m , that is, cause condensation or vaporization.

Finally, since t is a fraction of m by (18), we have

$$\left(\frac{\partial v}{\partial m}\right)_\phi \equiv \left(\frac{\partial v}{\partial t}\right)_\phi \cdot \left(\frac{\partial t}{\partial m}\right)_\phi = \frac{\lambda}{\varpi t} \cdot \frac{s + m \lambda \frac{d}{dt} \cdot \log. \varpi - \varpi t \frac{ds}{dt}}{s + m t \frac{d}{dt} \cdot \frac{\lambda}{t}};$$

and according as this is positive or negative will vaporization or condensation accompany expansion.

This case was first treated by Professor Clausius¹.

APPLICATION TO THE TEMPERATURES OF FUSION.

89. Fusion of ice. As ice contracts in the act of melting the melting-point will be lowered by an increase of pressure. The reasoning which led Professor James Thomson² to this conclusion may be thus exhibited. If compressed air at 0°C . be confined in a cylinder, all of non-conducting material except the bottom which is perfectly conducting and of no capacity for heat, and this cylinder be immersed in a small mass of water at 0°C ., the air will do work when allowed to expand at constant temperature and will at the same time absorb heat from the water, part of which will consequently be frozen. If

¹ *Pogg. Ann.* xcvi. (1856) 458, trans. *Phil. Mag.* [4] xii. (1856) 253.

² *Trans. R. S. E.* xvi. (1849) 575.

the water is enclosed in another piston-fitted cylinder, the formation of ice, tending to increase the volume, will increase the pressure and work can be obtained in allowing expansion till the pressure falls to its original value. If now work be spent in compressing the air to its original volume, the heat absorbed in the first operation will be restored to the water and reconvert into water the ice that was previously formed, work at the same time being done by the external pressure on the water during the accompanying contraction. Everything is now in its original state, and on the whole no heat has been expended; hence the excess of the work done by the water in expanding over that done on it during contraction must be equal to the excess of the work done on over that done by the air. The excess in the first case necessarily exists, as the pressure is least during the contraction; the excess in the second case can only exist if the air has a lower temperature during expansion than during compression: it must therefore be at a temperature below 0°C. when in contact with water freezing under greater than atmospheric pressure—and this temperature must be that of the water.

The calculation in this case of equation (9) is simple. The density of water at 0°C. relative to that at 4°C. is 0.999871, as deduced by M. Rosetti¹ from all the best observations; and therefore its absolute density in grams per cubic centimetre is 0.999884, as that of water at 4°C. is 1.000013 by § 1: hence $s' = 1.000116$. By Professor Bunsen's experiments² with his ice-calorimeter the relative density of ice at 0°C. is 0.91674 or its absolute density is 0.916752, whence

$$s = 1.090808 \quad \text{and} \quad u = -0.09069.$$

The same experiments give 80.025 for the latent heat at 0°C. in units which are equal to the hundredth part of the heat required to raise one gram of water from 0° to 100°C. , that is, to 1.011 calories; hence

$$\lambda = 80.025 \times 1.011 \times 41.55 = 3361.6 \text{ megalergs.}$$

¹ *Ann. de ch. et de phys.* [4] xvii. (1869) 375.

² *Pogg. Ann.* cxli. (1870) 7, trans. *Phil. Mag.* [4] xli. (1871) 165.

When heat (that is, work) is expressed in megalergs, pressure is expressed in megadynes; thus f denotes pressure in megadynes per square centimetre or in c. g. s. atmospheres. Also 0°C. is in absolute temperature $273\cdot7^{\circ}$: hence

$$\frac{df}{dt} = \frac{\lambda}{tu} = - \frac{3361\cdot6}{273\cdot7 \times 0\cdot09069} = - \frac{1}{0\cdot00738},$$

or the temperature of fusion is lowered by $0\cdot00738^{\circ}$ by every addition of one atmosphere to the pressure.

Professor Sir W. Thomson¹ confirmed this calculation by a piezometer of stout glass in which were placed an air-manometer formed of a straight glass tube and a delicate thermometer of sulphuric ether enclosed in a sealed glass tube for protection against compression. Sulphuric ether was chosen from having a small density $0\cdot736$ and a large expansion-coefficient $0\cdot001513$, so as not to deform the thermometer by its weight and yet give large readings for small differences of temperature. The thermometer scale contained $15\frac{3}{4}$ divisions to the centimetre, each equivalent to $0\cdot0078$ degree. The piezometer was filled with ice and water with a ring of lead to keep clear from ice that part of the thermometer where readings were expected. In two series of experiments the pressure when increased by $8\cdot1$ and $16\cdot8$ atmospheres, each of which corresponded to $29\cdot922$ inches of mercury at Glasgow or to $1\cdot0142$ c. g. s. atmospheres, produced a lowering in temperature of $7\frac{1}{2}$ and $16\frac{1}{2}$ divisions respectively, that is, of $0\cdot0586$ and $0\cdot1289$ degrees, or a lowering of $0\cdot00713$ and $0\cdot00756$ degrees (with a mean of $0\cdot00735$ or $1\frac{1}{8}$ degree) per additional c. g. s. atmosphere.



Fig. 39.

From the above then it is obvious that the highest temperature at which ice can exist is $0\cdot00738 \times 1\cdot0136 = 0\cdot00748^{\circ}\text{C.}$; for by § 11 its melting-point is 0°C. under the pressure of

¹ *Proc. R. S. E.* ii. (1850) 267, or *Phil. Mag.* [3] xxxvii. (1850) 123.

1.0136 atmospheres, and its possible temperature is highest in a vacuum.

Sir W. Thomson suggested the repetition of this experiment under great pressures as obtained by a Bramah press with a minimum thermometer to mark the corresponding melting-point. Professor Mousson¹ carried out this idea in a different way, directly shewing that by compression water may be maintained fluid at low temperatures. He first used two similar prisms of iron which when screwed together—their surfaces of contact being carefully worked plane and covered with caoutchouc to prevent leakage—had down their centre a cylindrical cavity whose lower end was firmly closed by a screw. At the top was another screw, the turning of which pressed down a piston-rod and compressed water with which the cavity was filled. The state of the water was examined, through two windows of thick glass let into the lower part, the test of fluidity being the mobility of a copper index in the bore. After compression the whole was placed in the cold winter air and the temperature of freezing determined: this was found to be between -3° and -5° c., the corresponding pressure, calculated from the above theoretical number, being about 540 atmospheres.

For higher pressures he used a prism of steel, as in the figure, with a cylindrical bore of 0.71 c. diameter; the lower part of the bore was closed by a copper cone pressed in by a strong screw; the upper part was slightly conical and was closed by a long plug *a* of copper pressed down by a steel piston by means of a strong screw and long lever. The copper by yielding to pressure made both ends water-tight, while the steel allowed any pressures to be used. The upper part was closed, and the whole reversed; a small brass rod *b* was then dropped in, and the bore filled with water. When exposed to the cold winter air at -9.5° c. the water congealed; the ice protruding from the cylindrical



Fig. 40.

bore was then removed, the copper cone put in and screwed

¹ *Pogg. Ann.* cv. (1858) 161.

up, and the whole again reversed and put into a freezing mixture at -18°C . The brass rod was obviously then uppermost, but by sufficient compression the ice was liquefied and the rod fell, as was shewn on removal of the lower screw and cone; for the rod issued first, followed by a cylinder of ice frozen on the reduction of the pressure. Hr. Mousson roughly estimated the compression at 0.134 and the pressure employed as not less than 13250 atmospheres: now the empirical formulae for the compression and expansion of water and ice indicate 1185 atmospheres only as the pressure corresponding to this compression; for 1 c.c. of ice at -9.5°C . is 0.99851 c.c. of ice at 0°C ., and this becomes 0.91548 c.c. of water at 0°C . under one atmosphere, or 0.8619 c.c. under 1185 atmospheres, or 0.866 c.c. of water at -18°C . under the same pressure: and again, the pressure required according to the theory is 2410 atmospheres only: hence though we are not perhaps justified in applying the above empirical formulae and theoretical number so far below 0°C ., we must regard the pressure in the above experiment as indefinite. It may of course have been much greater than was necessary to liquefy the ice.

Older experiments made by Major Williams¹ at Quebec seem to shew that the possibility of expansion is a necessary condition of congelation. A strong 13-in. iron shell, the thickness in different parts varying from $5\frac{1}{2}$ to $4\frac{1}{2}$ c., was filled with water and closed by an iron plug, of about 1.2 kilograms in mass, driven into the fuze-hole by a sledge-hammer, the sides of the plug being roughened by a file to secure greater firmness: it was then exposed to the cold. The most striking result was obtained with an out-door temperature of $-28\frac{1}{3}^{\circ}\text{C}$.: the plug was suddenly shot out at an elevation of 45° and thrown to a distance of 126 $\frac{1}{2}$ metres (indicating an initial velocity of at least 35 $\frac{1}{4}$ metres per second or 7450 megalergs of work), while a cylinder of ice, 22 c. long, was forced out of the hole, the expansion being about $\frac{1}{17}$ th of the original volume. On another occasion with an out-door temperature of $-24\frac{1}{2}^{\circ}\text{C}$., the plug being fastened internally by springs, the shell burst

¹ *Trans. R. S. E.* ii. (1786) 23.

and the ice came out of the cracks in thin plates like fins, in places 5 c. high. The temperatures given are not necessarily those of the water, and we cannot therefore estimate the internal pressures.

Professor Clausius¹ first used equation (8) to determine the rate of increase with the temperature of the latent heat of ice at its normal melting-point. By equations (4) we have

$$s' - s = (K' - K) + (L' - L) \varpi;$$

now s, L' are both very small, and so is *a fortiori* their difference; hence, though ϖ is about 135, we may write $K' - K$ for $s' - s$. We have $K' = 41.55$, and from M. Person's measures $K = 0.5037 \times 41.55 = 20.929$; hence $K' - K = 20.621$, and

$$\left[\frac{d\lambda}{dt} \right]_{0^\circ \text{C.}} = \frac{3361.6}{273.7} + 20.621 = 32.903,$$

or less than one per cent. of the value of λ at this temperature.

This result shews that λ diminishes with t when the pressure varies so as to preserve saturation. Before this demonstration M. Person² had concluded, since the specific heat of ice is less than that of water, that the latent heat diminishes when the freezing-point is lowered without increase of pressure by the fluid being kept perfectly still: this effect we may thus calculate³. If we cool a gram of water at constant pressure from 273.7° to t° , the heat given out is $\int_t^{273.7} K' dt$; if we could freeze the water at this temperature by absorbing the latent heat as fast as it becomes sensible—a process really impracticable, the failure of which however does not invalidate the reasoning—the heat given out is λ ; if the ice so formed is cooled to τ° , the heat given out is $\int_\tau^t K dt$; thus in these three processes heat equal to $\int_t^{273.7} K' dt + \lambda + \int_\tau^t K dt$ is given out; but the total change of intrinsic energy and external work, represented by this quantity, is entirely independent of the intermediate temperature

¹ *Pogg. Ann.* lxxxi. (1850) 168, trans. *Phil. Mag.* [4] ii. (1851) 548.

² *C. R.* xxx. (1850) 526.

³ Clausius' *Abhandlungen über die mechanische Wärmetheorie* (1864), i. 98.

t , as the pressure is constant: hence differentiating with respect to t we have

$$\frac{d\lambda}{dt} = K' - K.$$

A similar method, wherein the pressure is supposed to vary so as to preserve saturation, results in equation (6), thus justifying the procedure. In fact, in raising a gram of ice from τ° to t° always at saturation-point, in liquefying it at t° , and in raising the water so formed to 273.7° always at saturation-point, we expend heat $\int_{\tau}^t s dt + \lambda + \int_t^{273.7} s' dt$: during these processes external work $\int_{\sigma}^s f ds + f(s' - s) + \int_{s'}^{\epsilon} f ds'$ is done, if σ, ϵ are the initial and final volumes and s, s' correspond to the temperature t : now the total change of intrinsic energy is independent of the intermediate temperature t ; hence differentiating with respect to t the difference between the above quantities (which is this change of intrinsic energy) we get

$$\frac{d\lambda}{dt} + s - s' = (s' - s) \frac{df}{dt}.$$

If instead of considering equation (8) we take its integral in (16) and consider $s' - s$ constant and equal to $K' - K$, we have directly

$$\begin{aligned} \frac{\lambda}{t} &= 12.282 + 20.621 \log \frac{t}{273.7} \\ &= 47.481 (\log t - 2.1786). \end{aligned}$$

On this supposition λ is zero at temperature 150.9° , that is, 122.8 degrees below the normal melting-point: to this temperature will correspond a pressure of at least

$$\frac{122.8}{0.00738} + 1 = 16632 \text{ atmospheres.}$$

It would seem that at and below this temperature there is no distinction between the solid and liquid forms of water.

The phenomena of regelation (a better term for which would be *congelation*, as Professor James Thomson suggests) and glacier motion are easily explained by the lowering of the melting-point of ice by pressure.

90. Other experiments. Sir W. Thomson's prediction that an increase of pressure will raise the melting-point of those bodies that expand in melting was verified by the following experiments made independently by Professor Bunsen¹. A tube



Fig. 41.

AB of stout glass, 30 c. long, was drawn fine at both ends: the capillary part *AD*, about 4 c. long, was bent as in the figure, and the capillary part *BC*, about 46 c. long, was carefully calibrated. Both ends being open, mercury was sucked in and the end *C* sealed when the tube was full. Some mercury was driven out at *D* by heat; the space left on cooling was then filled by spermaceti, &c., and the end *D* sealed up. The end *C* having been now opened, mercury was driven out by heat; on the subsequent cooling air entered and the end *C* was again sealed so that *BC* could act as a manometer. The end *D* was then immersed in hot water and the spermaceti liquefied: it was allowed to cool, and the temperature of solidification was noted together with the corresponding

pressure, as indicated by the manometer, which increased with the length of the tube *AB* immersed. The temperature of fusion was found to increase with the pressure; it is approximately given for spermaceti in centigrade degrees by the formula (up to 158 atmospheres)

$$\Theta = 47.68 + 0.0207 p,$$

p denoting the pressure in atmospheres. Similar experiments with paraffin led to similar conclusions and a corresponding formula (up to 101 atmospheres)

$$\Theta = 46.27 + 0.0326 p.$$

Mr. Hopkins² extended these results by employing great pressures: the substance to be experimented on was placed in a $\frac{1}{4}$ in. brass tube *A* connected to a brass cylinder *B* full of oil, in which worked a piston *C*. Glass could not be used because of the great pressure, and even the brass had to be case-hardened to prevent escape of the liquid through its pores.

¹ *Pogg. Ann.* lxxxi. (1850) 562.

² *Rep. B. A.* (1854), ii. 56.

The liquefaction of the substance could not therefore be directly observed, but a small iron ball or, better, a magnetic needle in the tube at *D*, resting upon the substance while solid, deflected, an external magnetic needle; this deflection ceased when the ball fell on liquefaction of the solid, and the temperature of an oil-bath in which the whole instrument was immersed gave the temperature of fusion corresponding to the pressure during the experiment. The pressure was estimated by finding the weight W_1 which pushes in the piston against the external pressure through a certain small distance and the less weight W_2 which allows the piston to return through this distance, the atmospheric pressure and weight of the piston being included: if P is the total internal pressure on the piston and F the friction, we have $W_1 = P + F$, $P = W_2 + F$, whence $P = \frac{1}{2}(W_1 + W_2)$. The melting-points in centigrade degrees thus found are the following:—



Fig. 42.

Pressure in atmospheres.	Spermaceti.	Wax.	Stearine.	Sulphur.
1	51.1	64.7	67.2	107.2
538.4	60.0	74.7	68.3	135.3
820.5	80.3	80.3	73.9	140.6

According to these numbers the melting-point of wax is given by the formula $\Theta = 64.68 + 0.0188 p$: so simple a formula will not express the numbers found for the other substances. The difference between the result here found for spermaceti and that obtained by Professor Bunsen is due no doubt to difference in the specimens experimented on.

APPLICATION TO THE TEMPERATURES OF VAPORIZATION.

91. Maximum tension. M. Regnault¹ has experimentally determined the maximum tension at different temperatures

¹ *Mém. de l'Inst.* xxvi. (1862) 679.

of several vapours, and the results conform very exactly to the law represented by (2); the annexed table gives the constants as calculated by Professor Rankine¹, only so far altered that f may be expressed in c. g. s. atmospheres, t being measured from -274°C .

Vapour.	a	$\log b$	$\log c$	Range of Centigrade temperatures.	Range of pressures in centimetres of mercury at Paris.
Water	4.93934	3.1811430	5.0881857	-30 to $+230$	0.035 to 2094.5
Ether	4.25343	3.0596504	4.7065130	$+40.5$ to $+99$	76.2 414.7
Carbon bisulphide	4.02403	3.0520049	4.7078426		
Chloroform	2.93253	2.4007279	5.3919420	$+70$.	

92. Latent heat: total heat. In determining the latent heats of vapours M. Regnault found it more convenient to measure first the heat \mathfrak{h} required to raise unit-mass of a liquid from a standard temperature (which he took as 0°C .) under constant pressure to another temperature θ and there vaporize it, the constant pressure being the maximum tension of the vapour at θ : this he called the *total heat of the saturated vapour*—a not altogether satisfactory name; for if s_0 is the specific volume of the liquid at the standard temperature and under the given pressure, external work $f(s-s_0)$ will be done by the liquid in expanding and $f(s'-s)$ during vaporization, or $f(s'-s_0)$ in all, so that the actual heat put into the body is

$$\mathfrak{h}' = \mathfrak{h} - f(s' - s_0); \quad (19)$$

and if to this quantity is added (algebraically) that amount of heat which is required to raise the pressure at the constant standard temperature from a standard pressure (such as one atmosphere) to f , viz. $\int_1^f L_0 df$, we shall obtain a quantity that will exactly denote the actual excess of heat in the body when vaporized over what it contains in the standard state, and this

¹ *B. A. Rep.* (1854) ii. 58, or *Phil. Mag.* [4] viii. (1854) 530.

should properly be called the total heat of the vapour. This integral is however inappreciable for all liquids, so that h' may be taken as the real total heat. M. Regnault's results are summed up in the formula

$$h = a_1 + b_1\theta + c_1\theta^2,$$

the constants of which are given in the following table:—

Vapour.	a_1	b_1	c_1
Water	25200	12.673	
Ether	3905	18.698	0.02308
Carbon bisulphide	3740	6.067	0.01713
Chloroform	2784	5.713	

Now K being the specific heat at constant pressure of a liquid, $\int_0^\theta K d\theta$ is absorbed during the heating from 0° to θ° C., whence

$$\lambda = h - \int_0^\theta K d\theta. \quad (20)$$

M. Regnault has shewn that K varies inappreciably with the pressure and may be expressed by

$$K = a_2 + b_2\theta,$$

where a_2, b_2 are constants which for particular liquids are given in the table below. We have therefore

$$\int_0^\theta K d\theta = a_2\theta + \frac{1}{2}b_2\theta^2.$$

Liquid.	a_2	b_2
Water	41.550	0.00914
Ether	21.980	0.02457
Carbon bisulphide	9.774	0.00677
Chloroform	9.654	0.00422

From these tables we can by equation (20) at once find

$$\lambda = a_3 - b_3\theta + c_3\theta^2,$$

the constants being thus tabulated:—

Vapour.	a_3	b_3	c_3
Water	25200	28.877	-0.00457
Ether	3905	3.282	+0.01079
Carbon bisulphide	3740	3.707	+0.01374
Chloroform	2784	3.941	-0.00211

93. Table for water. Steam being the most important of all vapours, we have calculated the following table: s was found from (4) in which the values of K and L given in § 76 were used; it is expressed very well by the formula

$$s = 41.958 + 0.0047t - \frac{470}{t}:$$

s' was calculated by (8), u and s' by (9), λ' by (3): $f \frac{ds}{dt}$, which occurs in (14) and (15), was not calculated as its value is only 0.013 at 200° c. and may therefore be neglected.

The first two columns are temperatures and thus numbers (absolute temperature being the reciprocal of a ratio); columns 3-5 are pressures and are measured in c. g. s. atmospheres, *i.e.* in megadynes per square centimetre; columns 6-12 represent quantities of heat expressed in megacalergs; column 13 contains the ratios of similar magnitudes and thus numbers; columns 14-16 represent volumes measured in cubic centimetres.

TABLE OF VALUES FOR SATURATED STEAM.

θ	t	f	w	ϖt	λ	$-\frac{d\lambda}{dt}$	$\frac{\lambda}{t}$	λ'	s	$-s'$	$\int_{273}^t \frac{s}{t} dt$	$\frac{s-s'}{s}$	u	s	s'
0	273.7	0.00614	0.00044	0.1201	25200	28.877	92.072	23912	41.550	79.399	0.000	2.911	209905	1.00	209906
10	283.7	0.01222	0.00081	0.2303	24911	28.969	87.808	23589	41.042	75.135	1.493	2.804	108150	1.00	108151
20	293.7	0.02319	0.00143	0.4206	24621	29.060	83.830	23263	41.732	71.157	2.936	2.705	58538	1.00	58539
30	303.7	0.04207	0.00242	0.7338	24330	29.151	80.111	22935	41.824	67.187	4.336	2.612	33157	1.00	33157
40	313.7	0.07373	0.00391	1.2278	24038	29.243	76.626	22604	41.916	63.954	5.692	2.526	19578	1.01	19579
50	323.7	0.12267	0.00611	1.9772	23744	29.334	73.353	22271	42.006	60.692	7.010	2.445	12009	1.01	12010
60	333.7	0.19843	0.00922	3.0752	23451	29.425	70.277	21938	42.097	57.605	8.289	2.368	7626.0	1.02	7627.0
70	343.7	0.31085	0.01348	4.6346	23156	29.517	67.374	21603	42.187	54.794	9.534	2.297	4996.4	1.03	4997.4
80	353.7	0.47293	0.01920	6.7903	22861	29.609	64.635	21269	42.278	51.966	10.746	2.229	3366.8	1.03	3367.8
90	363.7	0.70070	0.02668	9.7019	22564	29.700	62.041	20934	42.366	49.375	11.925	2.165	2325.7	1.04	2326.7
100	373.7	1.01357	0.03626	13.5509	22267	29.791	59.586	20598	42.454	46.923	13.077	2.105	1643.3	1.04	1644.3
110	383.7	1.43417	0.04829	18.5304	21969	29.883	57.256	20269	42.540	44.599	14.199	2.048	1185.5	1.05	1186.6
120	393.7	1.98884	0.06315	24.8604	21669	29.974	55.039	19935	42.624	42.389	15.295	1.994	871.62	1.06	872.68
130	403.7	2.70768	0.08118	32.7737	21369	30.066	52.932	19603	42.707	40.291	16.365	1.943	652.01	1.07	653.08
140	413.7	3.62436	0.10277	42.5164	21068	30.157	50.925	19272	42.786	38.206	17.410	1.895	495.52	1.08	496.60
150	423.7	4.77610	0.12826	54.3431	20765	30.248	49.010	18940	42.860	36.398	18.432	1.849	382.12	1.09	383.21
160	433.7	6.20363	0.15797	68.5148	20463	30.340	47.186	18610	42.932	34.594	19.433	1.806	298.68	1.10	299.78
170	443.7	7.95076	0.19223	85.2932	20159	30.431	45.434	18280	43.002	32.867	20.411	1.764	236.36	1.11	237.47
180	453.7	10.06424	0.23128	104.9337	19854	30.523	43.760	17950	43.058	31.225	21.370	1.725	189.21	1.13	190.34
190	463.7	12.59325	0.27537	127.6887	19549	30.614	42.159	17621	43.111	29.662	22.310	1.688	153.10	1.14	154.24
200	473.7	15.58897	0.32466	153.7918	19242	30.706	40.621	17292	43.157	28.109	23.230	1.653	125.11	1.16	126.27
1															
	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16

94. Critical temperature. Examination of the numbers in column 9 shews that the real latent heat of steam may be very well expressed by the formula

$$\lambda' = 23924 - 33.2 \theta;$$

thus λ' diminishes as the temperature rises and is zero when $\theta = 720.6^\circ \text{C.}$ or $t = 994.3$. Hence above this temperature there is no difference between water in the liquid and the vapour forms, or 720.6°C. is for water what Dr. Andrews calls the *critical temperature*.

The formulae for other substances lead to a similar theoretical determination of their critical temperatures, but these as a rule lie so far beyond the limits within which the formulae have been justified that the results cannot be relied on; the calculated temperatures however agree very well with those experimentally determined. To MM. de la Tour¹, Drion², Andrews³, and Avenarius⁴ do we owe direct determinations: the last enclosed the liquid in greater or less quantities in hermetically-sealed glass tubes, and in all cases (even though the different masses used caused the pressures to be very different) it was found that over a certain temperature fixed for each substance there is no distinction between the liquid and vapour states, so that pressure alone will not cause a gas to liquefy—if, following Dr. Andrews, we reserve the term *gas* for a substance in the third state of aggregation and above the critical temperature, using the word *vapour* when the temperature is below this. Hr. Avenarius thus finds 292.5° , 276.1° , 246.1°C. as the critical temperatures for carbon tetrachloride, carbon bisulphide, and acetone respectively, while the temperatures calculated from M. Regnault's formulae are 346, 333, 272.

95. Specific heat of saturated vapour: temperature of inversion. The values of s' given in column 11 of the

¹ *Ann. de ch. et de phys.* [1] xxi. (1822) 127, 178; [1] xxii. (1823) 410; [1] xxiii. (1823) 267.

² *Ann. de ch. et de phys.* [3] lvi. (1859) 5.

³ *Phil. Trans.* clix. (1869) 575.

⁴ *Pogg. Ann.* cli. (1874) 303.

preceding table are summed up exceedingly well in the formula

$$s' = 42.136 - \frac{33280}{t};$$

thus s' is zero when $t = 789.8$ or at the temperature 516.1°C. , being positive for all higher and negative for all lower, and thus all ordinary, temperatures. This fact was discovered almost simultaneously by Professors Rankine¹ and Clausius² in 1850. The interpretation of the negative sign is that in order to keep saturated a dry vapour which is *rising* both in temperature and pressure we must *withdraw* heat, otherwise the vapour will become superheated: thus if the vapour expands so that its pressure diminishes we must communicate heat in order to keep it saturated, otherwise part of the vapour will condense to supply the requisite heat, and this is the case with steam for all temperatures below 516.1°C. , which is called the *temperature of inversion*; above this temperature compression will cause condensation and expansion vaporization.

M. Hirn³ gave an experimental demonstration in 1862 of the condensation accompanying a sudden adiabatic expansion of dry saturated steam, and thus proved the negative sign of s' at low temperatures: he allowed steam to pass gently from a boiler, where it was generated under 5 atmospheres pressure, through a copper cylinder, 200 c. long and 15 c. in diameter, the ends of which were closed by plates of glass, until all air and condensed water had been driven out and the sides had attained the temperature of the steam; the exit-stopcock of the cylinder was then shut, and, the cylinder being full of dry saturated steam, the connection with the boiler was cut off and the exit-stopcock suddenly opened; the pressure at once fell, and the cylinder, which had previously appeared perfectly transparent to an observer looking along its axis, became perfectly opaque from the formation of a cloud; this cloud

¹ *Trans. R. S. E.* xx. (1850) 171.

² *Pogg. Ann.* lxxix. (1850) 391, trans. *Phil. Mag.* [4] ii. (1851) 14.

³ *Bulletin de la Soc. industr. de Mulhouse*, cxxxiii. (1862) 129; *Cosmos*, xxii. (1863) 413.

however soon disappeared, heat being supplied by the vessel as it cooled from 152°C . (the temperature of saturated steam under 5 ordinary atmospheres) to 100°C . (the temperature under 1 atmosphere).

M. Cazin¹ improved this apparatus by connecting the cylinder with another in which a piston was moveable, and placing the whole in an oil-bath the temperature of which could be varied at will: saturated vapour in the one could then be allowed to suddenly expand into the other, or when filling both could be suddenly compressed by the motion of the piston. A cloud was always formed when steam expanded but never on its compression, and with carbon bisulphide the same occurred; on the contrary, as noticed earlier by M. Hirn, ether vapour never condensed during expansion but always on compression, shewing that its temperature of inversion is below ordinary temperatures; further, the temperature of inversion appeared to be between 125° and 129°C . for chloroform, and for benzene between 115° and 130°C . These results are in keeping with theory, M. Regnault's formulae giving 790.2° , -113° , 123.5° , 100°C . for the temperatures of inversion of carbon bisulphide, ether, chloroform, and benzene respectively.

96. Adiabatic expansion. In the above experiments the vapours expanded nearly adiabatically; it may therefore be well by a single example to illustrate the general action.

A mixture at 150°C ., half water and half steam, is enclosed in a non-conducting cylinder and then allowed to expand by pressing out a piston; what happens?

For water both ϖ and $\frac{s}{t}$ increase with t and therefore $(\frac{\partial v}{\partial t})_{\phi}$ is always negative; hence $(\frac{\partial m}{\partial v})_{\phi}$ is of opposite sign to $(\frac{\partial m}{\partial t})_{\phi}$, and vaporization or condensation accompany expansion according as

$$1 - \frac{s - s'}{s} m$$

is positive or negative. In the given case this binomial is

¹ C. R. lxi. (1866) 56.

$1 - \frac{1.849}{2} = +0.075$, and vaporization at first occurs, but continues only till the binomial becomes zero, or

$$m = \frac{s}{s - s'}.$$

Now initially

$$m_0 = 0.5, \quad \frac{\lambda_0}{t_0} = 49.010, \quad \int_{273.7}^{423.7} \frac{s}{t} dt = 18.432,$$

so that by (18)

$$\begin{aligned} \frac{m\lambda}{t} + \int_{273.7}^t \frac{s}{t} dt &= (0.5 \times 49.010) + 18.432 \\ &= 42.937, \end{aligned}$$

or, on substitution of the above value of m ,

$$\frac{s}{s - s'} \cdot \frac{\lambda}{t} + \int_{273.7}^t \frac{s}{t} dt = 42.937.$$

The table in § 93 gives 42.897 and 43.607 for the values of this sum at 120° and 130° C., between which temperatures therefore θ lies; and, as the difference $43.607 - 42.897 = 0.710$ corresponds to an increase of 10 degrees, the difference

$$42.937 - 42.897 = 0.040$$

corresponds to 0.6 degree, whence $\theta = 120.6^\circ$ C. Further, the value of $\frac{s - s'}{s}$ at this temperature is

$$1.994 - \frac{0.6}{10}(1.994 - 1.943) = 1.991,$$

and m therefore becomes $\frac{1}{1.991} = 0.5023$: also the specific volume $mu + s$, which was initially

$$(0.5 \times 382.12) + 1.09 = 192.15 \text{ c.c.},$$

becomes $(0.5023 \times 855.61) + 1.06 = 430.83 \text{ c.c.}$;

and the work that has been done during the expansion per gram of the mixture is

$$191.06 \times 49.5670 - 429.77 \times 23.2607 + \frac{1}{2}(42.860 + 42.629) \times (150 - 120.6) = 730.2 \text{ megalergs}$$

by (15), if the mean value of s between 150° and 120.6° C. is used in the integral.

As the expansion goes on the temperature will still fall, but vapour will be continuously condensed, and the mixture will again become half water half steam when again

$$\frac{1}{2} \frac{\lambda}{t} + \int_{273.7}^t \frac{s}{t} dt = 42.937.$$

Now at 100° and 90° C. this sum is 42.870 and 42.946 respectively, so that the required temperature is 91.3° C.; the specific volume also becomes $(0.5 \times 2213.6) + 1.04 = 1108$ c.c., and the external work is increased by

$$429.77 \times 23.2607 - 1108 \times 9.4057 \\ + \frac{1}{2} (42.529 + 42.377) \times (120.6 - 91.3) = 820.6 \text{ megalergs.}$$

97. Density of saturated vapour. It was formerly assumed, for want of experimental data, that vapours conform to the gaseous laws even up to their points of saturation: thus the theoretical density of steam (H_2O) under one megadyne pressure at 0° C. (if it could so exist) being

$$\frac{1}{2} \{ (2 \times 0.0000884) + 0.0014107 \} = 0.0007937$$

grams per cubic centimetre by M. Gay Lussac's law, since 0.0000884, 0.0014107 are the densities of hydrogen and oxygen respectively under the same circumstances—which agrees very well with M. Regnault's experimental value 0.623 for its density in a superheated state relative to air, or in the above hypothetical state $0.623 \times 0.00127592 = 0.0007949$ g. per c.c.—the specific volume of steam was calculated from the formula

$$\frac{pv}{t} = -\frac{1}{273.7} \times \frac{1}{0.0007937} = 4.603,$$

which was extended even to the state of saturation, so that

$$\frac{fs'}{t} = 4.603. \quad (21)$$

Hr. Clausius first shewed¹ that grave error was introduced by this assumption, and, having deduced the values of s' for steam at different temperatures by the method we have followed, gave the empirical formula

$$\rho' = \frac{a'}{b - c\theta}$$

¹ *Pogg. Ann.* lxxix. (1850) 520, trans. *Phil. Mag.* [4] ii. (1851) 116.

for the density ρ' of saturated steam at temperature θ° c. relative to air, a', b, c being constants: as the density of air at θ° c. and under the pressure f megadynes is $\frac{0.00127592 f}{1 + 0.00367 \theta}$, the absolute density ρ of saturated steam is given by

$$\rho \equiv \frac{1}{s'} = \frac{af}{(b - c\theta)(d + \theta)}, \quad (22)$$

where the constants, expressed in our units, are

$$a = 6.2899, \quad b = 30.087, \quad c = 1.0072, \quad d = 272.48.$$

Hr. Zeuner has suggested the formula¹

$$\rho = af^b, \quad (23)$$

as at once more simple and exact, and it represents the reciprocals of the numbers we have given in column 14 of the table in § 93 extremely well if the constants are $a = 0.000597$, $\beta = 0.942$. This gives

$$f^\beta s' = \gamma, \quad (24)$$

where γ is a constant, which in the case of steam is 1675.

Or again, since s is in general very small compared with s' , equation (3) may be written

$$fs' = \lambda - \lambda', \quad (25)$$

or in the case of steam

$$fs' = 1276 + 4.323 \theta - 0.00457 \theta^2.$$

In 1860 Sir W. Fairbairn and Mr. Tate² made direct experiments on the density of saturated steam by means of the *saturation-gauge* of the latter. This in its theoretical form consists of two globes A and B void of air but containing some liquid and its vapour, and connected by a bent tube containing mercury; if A contains less liquid than B , and the whole is placed in a bath the temperature of which is continuously raised, the level of the mercury in the tube will remain unchanged until all the liquid in A is vaporized; further heating will then superheat the vapour in A , and the mercury will rise at a , as at the same temperature the rate of increase of pressure is greater for



Fig. 43.

¹ *Grundzüge der mechanischen Wärmetheorie*, 2^{te} Auflage (1877), 266.

² *Phil. Trans.* cl. (1860) 185; clii. (1862) 591.

saturated than for superheated vapours. If then we know the mass of liquid introduced into *A*, and we note the volume occupied by its vapour and the temperature when the mercury at *a* begins to rise, we can determine by division the corresponding density. By using a bath of the vapour experimented upon there can be no danger of bursting the globes, as the pressures will be the same within and without, so long as saturation continues.

The actual apparatus used is represented in the figure: a Torricellian vacuum was made in the globe *A* and a small glass globule *a* inserted, the globule having previously been filled

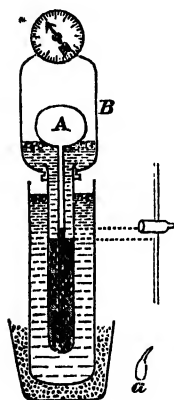


Fig. 44.

with warm water and allowed to cool with its stem dipping in mercury, so that it was safely closed without any explosion being necessary, as in M. Gay Lussac's method: the globe was heated in a water-bath *B* provided with a manometer and a safety valve, and the lower part of the stem was heated as nearly as possible to the same temperature in an oil-bath standing on a sand-bath, the mercury levels being observed by a cathetometer. The vapour was always first superheated so as to overcome the force of cohesion between the water and the glass, and this force did not again come into play until the glass was again wetted by the vapour becoming saturated. The ex-

periments ranged from 58.2° to 144.7° C., and led to the formula

$$s' = a + \frac{b}{f+c}, \quad (26)$$

where the constants (expressed in our units) are

$$a = 25.62, \quad b = 1677.61, \quad c = 0.02440:$$

from this we deduce $\rho = a - \frac{\beta}{f+\gamma}, \quad (27)$

where $a = 0.039032, \quad \beta = 2.556, \quad \gamma = 65.505.$

Dr. Herwig¹ has lately made elaborate experiments on the

¹ *Pogg. Ann.* cxxxvii. (1869) 19, 592; cxli. (1870) 83.

behaviour of vapours with regard to the gaseous laws, and arrives at the curious conclusion that if P, V represent the pressure and specific volume of a vapour at temperature t in the perfect state and f, s' its pressure and specific volume at the same temperature when saturated, then in all cases

$$\frac{PV}{fs'} = 0.0595\sqrt{t}, \quad (28)$$

whence, if ρ' is the density of the vapour in the perfect state relative to air,

$$fs' = \frac{2.8725 t}{0.0595 \rho' \sqrt{t}} = \frac{48.28}{\rho'} \sqrt{t},$$

or
$$\frac{fs'}{\sqrt{t}} = \frac{48.28}{\rho'}. \quad (29)$$

The substances experimented on were alcohol, chloroform, carbon bisulphide, ether, ethyl bromide, and water: for the latter $\rho' = 0.623$, so that $\frac{fs'}{\sqrt{t}} = 77.49$.

The apparatus used consisted of a graduated glass cylinder A connected with a wider one B which communicated with a manometer C through a drying tube D ; a branch tube E led to an air-pump when required. Precautions were taken to exclude damp from A by using warm mercury in filling it initially: the small amount of air also that entered, when a glass globule containing the liquid was introduced was carefully determined by varying the pressure and temperature before exploding the globule. The range of temperatures was not great; in the case of water they varied only from 40° to 95° C.

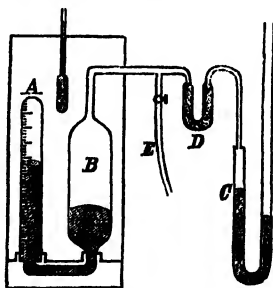


Fig. 45.

Hr. Herwig arrived also at another curious result. M. Regnault¹ found an apparent exception to the law $f = F(t)$ in the case of ether-vapour if air be present in any quantity, and

¹ *Mém. de l'Inst.* xxvi. (1862) 679.

Hr. Herwig shewed that when condensation begins, even in the absence of air, the manometer indicates a less tension than is given by M. Regnault's formula, and that as the volume is lessened condensation continues, the pressure gradually increasing up to M. Regnault's maximum; he explains it 'by the assumption of a force of adhesion acting strongly between the walls of the apparatus (*sc.* both the glass and the mercury) on the one hand and the ether on the other, by means of which in passing from a highly superheated state to a smaller volume the vapour begins to condense before reaching the volume that would correspond to purely saturated vapour were no such force existing: on the contrary, at a very great distance from the ideal limits of saturation up to the superheated state such an influence can no longer be assumed.'

If fs' is calculated from the equation (28), the maximum tension as determined by M. Regnault being then substituted for f , a value of s' is obtained which is exactly the volume which the vapour is observed to occupy just before condensation begins: whence the real tension of the vapour is most probably constant throughout the condensation, and the force of adhesion that acts at any moment is equal to the difference between the maximum and the indicated tensions.

The same action occurs with water and with ethyl bromide, being also slightly traceable in carbon bisulphide.

M. Hirn¹ has experimented on superheated steam, and Hr. Ritter² shews that his results can be summed up in the formula (suggested by certain theoretical considerations)

$$t = \frac{pv}{R} + \frac{S}{pv^{\frac{2}{3}}}, \quad (30)$$

where $R = 4.653$, $S = 1043800$.

This also represents the numbers of § 93 much better than any of the foregoing formulae, as is shewn by the subjoined table wherein the specific volumes of saturated steam, calculated by the different methods, are compared: it may therefore be taken as the characteristic equation of steam.

¹ *Théorie mécanique de la Chaleur*, 3^{ème} éd. (1875) ii.

² *Pogg. Ann.* [2] iii. (1878) 447.

θ	Gaseous laws (21).	Clausius' formula (22).	Zeuner's formula (23).	Formula (25).	Fairbairn and Tate's (26).	Herwig's (29).	Ritter's (30).	Tabular values, § 93.
40	19719	19695	19656	19684	17183	18743	19604	19579
60	7740.9	7605.2	7685.3	7655.7	7528.7	7133.8	7640.3	7627.0
80	3442.5	3354.7	3437.1	3364.5	3373.2	3081.5	3368.8	3367.8
100	1697.1	1638.2	1653.9	1640.6	1616.2	1477.9	1644.7	1644.3
20	911.18	869.75	876.44	869.43	833.29	773.08	873.52	872.68
40	525.41	483.71	498.02	494.40	459.78	434.87	497.83	496.60

APPLICATION TO THE TEMPERATURES OF SUBLIMATION.

98. Sublimation. Experimental data are entirely wanting with regard to the direct transformation into vapour of a solid substance: were these at hand, we might apply to them all the above formulae.

The pressure of saturated steam in contact with ice between 0° and -32° c. has certainly been measured by M. Regnault, who has expressed his results by the formula

$$f = a + ba^{\theta},$$

where $a = 0.0001072$, $b = 0.006255$, $\alpha = 1.080$.

THERMAL LINES OF THE SATURATED CONDITIONS.

99. Thermal lines. The *isothermals* are obviously isopiestic, since the pressure is a function of the temperature only, and their length is $s' - s$; now for vapours in contact with their liquid s increases while s' diminishes as the temperature rises, and therefore this length must vanish at some temperature—the critical temperature—corresponding to a pressure above which there is no distinction between the liquid and vapour states, as shewn in § 94. We have no data for the other states of saturation and cannot therefore draw any further conclusion, though § 89 seems to shew that at -122.8° c. and under at least 16632 atmospheres pressure there is no difference

between the solid and liquid forms of water. The external work that is done in passing along an isothermal is

$$\int_1^2 f dv = f(v_2 - v_1) = fu(m_2 - m_1).$$

The *isenergies* (or *isodynamics*) are, by (15), given by

$$(v-s) \left(\frac{d}{dt} t - f \right) + \int_{t_0}^t \left(s - f \frac{ds}{dt} \right) dt = \text{const.},$$

wherein s , t , s must all be expressed in terms of f . As we only know the relations between these quantities empirically in a few cases and under limited conditions, we cannot find a general expression for all substances: but examination of the values of this function as deduced from the table in § 93 has led Hr. Zeuner¹ to the conclusion that the isenergies, at least for steam in contact with water, are given by

$$fv^n = \text{const.},$$

the value of n for water being 1.0456. The isenergies must be limited by the curves that bound the portion of the diagram which correspond to the saturated state: their prolongations over these lines represent the intrinsic energy of the body as a superheated vapour or as a vapourless liquid.

These bounding curves may be called by the names given to their water-types by Professor Maxwell; viz. (1) the *ice line* separating the solid from the liquid state, (2) the *steam line* separating the liquid from the gaseous state, (3) the *hoar-frost line* separating the gaseous from the solid state. Theory does not indicate the form of these lines, but we gather from (23) that the steam line for water at least is given by

$$fv^v = \text{const.},$$

v being 1.0616 for water.

The curves representing the states wherein m is constant—called by Hr. Zeuner the *lines of constant vapour-mass* for one species of saturation—are, by (13), given by

$$\phi + \int_{t_0}^t \frac{s}{t} dt - m \frac{\lambda}{t} = \text{const.};$$

¹ *Grundzüge &c.*, p. 306.

these are more or less similar to the last-mentioned lines which are their limiting cases.

The *isentropics* or *adiabatics* are by (13).

$$\frac{m\lambda}{t} + \int_{t_0}^t \frac{s}{t} dt = \text{const.},$$

as in § 88. Professor Rankine has attempted to express them in the form $f v^\mu = \text{const.}$,

where μ is a constant; but Hr. Zeuner shews that μ is a function of m . It is easy to see that for such vapours as steam which condense on adiabatic expansion the isentropics cut the steam line S as in 1, since as the volume increases the vapour changes from the superheated to the saturated state, and that for vapours like ether, which behave in the reverse manner, the isentropics cut as in 2.

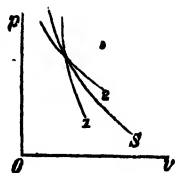


Fig. 46.

Chapters VI and VII in Professor Maxwell's 'Theory of Heat' should be studied on the subjects of this article.

100. Triple point. We are led to very interesting results if we consider the projections of the real ice, steam, and hoar-frost lines of water-substance on the plane of $p\lambda$. Hr. Kirchhoff¹ shewed in 1858 that these projections of the steam and hoar-frost lines are not continuous, as M. Regnault thought, but intersect at an angle which is re-entrant downwards. The assumption being made that there is some temperature t_0 at which both ice and water can exist together and at which the steam formed over ice is exactly identical in condition with that formed over water—this temperature being about 0.0074° c., as the pressure will be only about 0.00614 instead of 1 atmosphere—it follows that, when unit-mass of ice at this temperature is directly transformed into vapour, its intrinsic energy is increased by exactly the same amount as if the transformation were first into the liquid and then into the vapour state. Now during vaporization at temperature t_0 from the solid state, the

¹ Pogg. Ann. ciii. (1858) 206.

increase of intrinsic energy is $u_0'(\varpi_0' t_0 - f_0)$ by (9), the accents denoting the process of sublimation; but during the liquefaction the increase of intrinsic energy is $\lambda_0 - f_0 u_0''$, if λ_0 is the latent heat of fusion at the same pressure f_0 and u_0'' the change of volume, and during the subsequent vaporization the increase of intrinsic energy is $u_0(\varpi_0 t_0 - f_0)$; hence

$$u_0'(\varpi_0' t_0 - f_0) = \lambda_0 - f_0 u_0'' + u_0(\varpi_0 t_0 - f_0):$$

but u_0' is equal to $u_0 + u_0''$, and it may be taken equal to u_0 , as u_0'' is less than its 200,000th part; thus the equation becomes

$$\varpi_0' - \varpi_0 = \frac{\lambda_0}{u_0 t_0}.$$

Here $t_0 = 273.7$ sensibly, $\lambda_0 = 3361.6$ (see § 89), $u_0 = 209905$ (see table, § 93); whence $\varpi_0' - \varpi_0 = 0.0000585$. Hr. Kirchhoff remarks:—‘This difference is too small to be safely inferred from Regnault’s experiments. It is interesting however to remark that a difference of the same sign and order of magnitude as the theory requires is furnished by the numbers which Regnault gives as the results of his experiments.’ For the empirical formulae give $\varpi_0' = 0.000482$, $\varpi_0 = 0.000439$, whence $\varpi_0' - \varpi_0 = 0.000043$. The lines therefore cut each other, and the angle of intersection is re-entrant downwards as $\varpi_0 < \varpi_0'$.

Professor James Thomson¹ has pointed out that the ice line must also pass through this point P , which he therefore calls the *triple point*: thus in the diagram, which is of course not drawn to scale, PC may be taken as the steam line which ends at the critical point C , PA as the hoar-frost line, PB as the ice line, the length

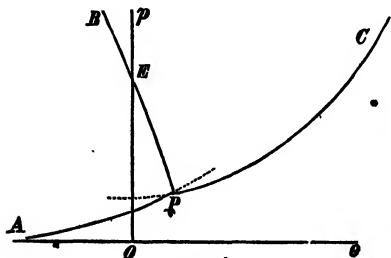


Fig. 47.

OE representing 1 atmosphere. Following Sir W. Thomson’s

¹ *B. A. Rep.* (1871) ii. 30; (1872) ii. 24; *Proc. R. S.* xxii. (1873) 27.

suggestion he has further applied equation (9) in the form

$$\frac{\varpi'_0}{\varpi_0} = \frac{\frac{\lambda'_0}{u'_0 t_0}}{\frac{\lambda_0}{u_0 t_0}} = \frac{\lambda'_0}{\lambda_0},$$

with our former notation and considering as before $u'_0 = u_0$. Now at 0°C . $\lambda_0 = 25200$ (see § 93), and

$$\lambda'_0 = 3361.6 + 25200 = 28561.6,$$

being equal to the sum of the heat required to melt and then vaporize the ice: thus $\frac{\varpi'_0}{\varpi_0} = 1.133$, M. Regnault's empirical formulae giving the ratio 1.10. Hence a new proof of Hr. Kirchhoff's theorem.

Joining together these two theoretical results

$$\varpi'_0 - \varpi_0 = 0.0000585, \quad \frac{\varpi'_0}{\varpi_0} = 1.133,$$

we find $\varpi'_0 = 0.000498$, $\varpi_0 = 0.000440$, which are nearly the values given by experiment.

This reasoning applies to substances in general. A full and interesting discussion of the form and sections of the characteristic surface representing the different states of water has lately been made by Hr. Ritter¹: a general representation of the properties of a substance by means of a surface, the coordinates of which are the volume, entropy, and intrinsic energy of the body, has been given by Professor Gibbs², and should be studied in Professor Maxwell's 'Theory of Heat,' p. 195.

¹ *Pogg. Ann.* [2] ii. (1877) 273, trans. *Phil. Mag.* [5] v. (1878) 202.

² *Trans. Acad. of Sciences of Connecticut*, ii. (1871) 309.

CHAPTER IX.

On the Flow of Fluids.

161. General formula. In 1856 Sir W. Thomson and Dr. Joule¹ extended the reasoning of the former, which has been given in § 71, to the case in which fluids issue from an orifice with a sensible velocity. If the mean velocity of unit-mass of the fluid is changed from ν_0 at the section where the pressure is p_0 to ν at the section where the pressure is p , kinetic energy $\frac{1}{2}(\nu^2 - \nu_0^2)$ has been imparted to it; and if moreover it has had to rise or fall through a height h in reaching the position where its velocity is ν , energy equal to $\pm gh$ (where g is the acceleration of gravity) has been absorbed in the process: thus equation (3), § 71, becomes more generally, if H' is the energy turned into heat by means of friction,

$$E - E_0 = H - \Sigma + p_0 v_0 - pv - \frac{1}{2}(\nu^2 - \nu_0^2) \mp gh - H',$$

or $\frac{1}{2}(\nu^2 - \nu_0^2) = (E_0 - E) + (p_0 v_0 - pv) + (H - H') - \Sigma \mp gh. \quad (1)$

Now the energy that is turned into heat by friction is always very small per unit-mass of fluid that escapes, so that H' may be neglected: also Σ is either zero or very small, and as a rule the efflux occurs approximately adiabatically, so that H is also zero: hence the equation becomes

$$\frac{1}{2}(\nu^2 - \nu_0^2) = (E_0 - E) + (p_0 v_0 - pv) \mp gh, \quad (2)$$

the last term being comparatively negligible in the case of gases, but not in the case of liquids. We may further substitute the value of $E_0 - E$ given in (25), § 57, and obtain

$$\begin{aligned} \frac{1}{2}(\nu^2 - \nu_0^2) \\ = \int_{\nu_0}^{\nu} p \, dv + p_0 v_0 - pv - t \frac{\partial}{\partial t} \int_{\nu_0}^{\nu} p \, dv - \int_{t_0}^t k_{v_0} \, dt \mp gh. \end{aligned} \quad (3)$$

¹ *Proc. R. S.* viii. (1856) 178.

102. Incompressible fluids. Looking upon liquids as incompressible, so that $dv = 0$, and remembering that there will be no change of temperature if no compression is effected and no heat added, or that $dt = 0$, we see that the equation becomes in this case

$$\frac{1}{2}(v^2 - v_0^2) = (p_0 - p)v_0 \mp gh, \quad (4)$$

the upper or lower sign of the last term being taken according as the liquid rises or falls to the position where its velocity is v : if then there is no initial velocity we have

$$\frac{v^2}{2} = (p_0 - p)v_0 \mp gh, \quad (5)$$

which is M. Bernoulli's formula for the velocity of efflux of liquids.

103. Compressible fluids. We shall consider a perfect gas as a type of compressible liquids, and examine two cases.

(1) *Efflux at constant temperature.* In this case

$$pv = p_0 v_0, \quad \int_{v_0}^v p dv = p_0 v_0 \log_e \frac{p_0}{p}, \quad \text{and} \quad \frac{\partial}{\partial t} \int_{v_0}^v p dv = 0;$$

hence, if H is the heat added to maintain this constancy of temperature and if the initial velocity of the gas is zero,

$$\frac{v^2}{2} = p_0 v_0 \log_e \frac{p_0}{p} + H. \quad (6)$$

Supposing that no heat is required to keep the temperature constant or $H = 0$, we obtain M. Navier's formula which was deduced from the improbable hypothesis of parallel sections.

(2) *Efflux without receiving or losing heat.* In this case,

$$pv^\kappa = p_0 v_0^\kappa, \quad E_0 - E = k(t_0 - t), \quad \text{by (53), § 63,}$$

$$p_0 v_0 - pv = \frac{p_0 v_0}{t_0} (t_0 - t) = (K - k)(t_0 - t):$$

hence equation (2) becomes, if the initial velocity is zero,

$$\left. \begin{aligned} \frac{v^2}{2} &= K(t_0 - t), \\ &= K t_0 \left\{ 1 - \left(\frac{p}{p_0} \right)^{\frac{\kappa-1}{\kappa}} \right\}, \\ &= \frac{\kappa}{\kappa-1} p_0 v_0 \left\{ 1 - \left(\frac{p}{p_0} \right)^{\frac{\kappa-1}{\kappa}} \right\}, \end{aligned} \right\} \quad (7)$$

by (62) and (64), § 63. The second formula in (7) was first deduced in another way by Hr. Weisbach¹ in 1855.

If so much friction is caused against the orifice or walls of the containing tube or vessel that H' cannot be neglected, t will be greater and therefore u smaller than in the other case. The variation in the velocity of efflux with the form of the ajutage is due to the variation in the frictional effects by reason of the variation of the form and dimensions of the *vena contracta*.

The velocity increases as p diminishes in comparison with p_0 , but the formula gives

$$\sqrt{2Kt_0} \text{ or } \sqrt{\frac{2\kappa}{\kappa-1} p_0 v_0}$$

as the limiting velocity which cannot be surpassed.

104. Saturated fluids. Substituting for $E-E_0$ from (14), § 86, we get from equation (2), if the initial velocity is zero and the fluid remains always saturated,

$$\frac{v^2}{2} = (f_0 v_0 - f v) - m(\lambda - f u) + m_0(\lambda_0 - f_0 u_0) - \int_{t_0}^t (s - f \frac{ds}{dt}) dt, \quad (8)$$

with the further equation of condition

$$\frac{m\lambda}{t} - \frac{m_0\lambda_0}{t_0} + \int_{t_0}^t \frac{s}{t} dt = 0, \quad (9)$$

by (18), § 88.

If we consider the efflux of saturated vapour only, considering it to remain saturated, so that $m_0 = 1$, $v_0 = s_0'$, we have

$$\left. \begin{aligned} \frac{v^2}{2} &= \lambda_0 + f_0 s_0 - f v - m(\lambda - f u) - \int_{t_0}^t (s - f \frac{ds}{dt}) dt, \\ \frac{m\lambda}{t} &= \frac{\lambda_0}{t_0} - \int_{t_0}^t \frac{s}{t} dt \end{aligned} \right\} \quad (10)$$

if condensation occurs during the efflux, and

$$\left. \begin{aligned} \frac{v^2}{2} &= (\lambda_0 + f_0 s_0) - (\lambda + f s) - \int_{t_0}^t (s - f \frac{ds}{dt}) dt, \\ \frac{\lambda}{t} &= \frac{\lambda_0}{t_0} - \int_{t_0}^t \frac{s}{t} dt \end{aligned} \right\} \quad (11)$$

¹ *Ingenieur- und Maschinenmechanik*, 3^{te} Aufl. i. 821.

if no condensation occurs. In the latter case we obtain the more simple equation

$$\frac{v^2}{2} = h_0 - h \quad (12)$$

by (20), § 92, if h_0, h denote the total heat of the vapour in its initial and final states, $(\int_0 s_0 - \int s)$ and $\frac{ds}{dt}$ being neglected by reason of their smallness and κ being replaced by its approximate value K .

For all known liquids h increases with t and the temperature diminishes during adiabatic expansion: hence $h_0 - h$ is a positive quantity, and (12) contains no contradiction. Still the issuing jet enlarges rapidly beyond the contracted vein, and consequently its velocity diminishes equally rapidly from the same section; hence v becomes negligible before the vapour mixes with the air, and thus, $h_0 - h$ being neither zero nor negative, the hypothesis of the persistence of saturation is untrue: and, further, there cannot be condensation, since, m being a fraction, the right-hand expression of (10) is greater than that of (11) which we have just shewn is itself too great. Hence at a short distance from the orifice the issuing vapour must be *superheated* and *dry*, though close to the orifice where v is great it is saturated and partly condensed—the superheating and re-vaporization of the condensed droplets being due to the friction of the particles among each other and the transformation into heat of their energy of motion. This is, Sir W. Thomson's¹ explanation of the well-known facts that, while the hand is scalded if placed close to an orifice from which high-pressure steam is escaping, it experiences only a pleasant sensation of warmth if held a little distance off in the jet, and that if the energy of motion has been utilized in actual work—as in driving the piston of a steam-engine—the steam afterwards issues saturated and therefore scalds. This explanation was

¹ *Phil. Mag.* [3] xxxvii. (1850) 386: see also Clausius' memoir, *Pogg. Ann.* lxxxii. (1851) 263, trans. *Phil. Mag.* [4] i. (1851) 398, and the notes *Phil. Mag.* [4] i. (1851) 474, ii. (1851) 139, 273.

given afresh a little later by Hr. Clausius, who had misunderstood Professor Thomson's expression 'fluid friction.'

The temperature of the vapour t' before mixing with the air may thus be approximately determined. We may suppose that the vapour expands, always remaining saturated and dry, till its tension becomes equal to the external pressure, its temperature falling from t_0 to t corresponding to this last pressure and its velocity becoming v , and that its kinetic energy is then immediately and totally transformed into heat, bringing it at constant pressure into the superheated and dry state at temperature t' with no velocity of motion. K' being its specific heat in the superheated state, $\int_t^{t'} K' dt$ is the heat absorbed in this superheating, and therefore from (12)

$$h_0 - h = \frac{v^2}{2} = \int_t^{t'} K' dt. \quad (13)$$

In the case of steam $K' = 0.4805 \times 41.55 = 19.965$,

and $h = 25200 + 12.673 \theta$;

hence taking θ_0 , θ , θ' as the temperatures centigrade corresponding to t_0 , t , t' , we have

$$12.673(\theta_0 - \theta) = 19.965(\theta' - \theta),$$

or

$$\theta' - \theta = \frac{7}{11}(\theta_0 - \theta).$$

Thus, if the steam is generated at 150°C. where the pressure is 4.7761 atmospheres and escapes into the open air where the pressure is 1.0136 atmospheres, so that $\theta = 100^\circ \text{C.}$, we find

$$\theta' = 100 + \frac{7}{11}(150 - 100) = 132^\circ \text{C.}$$

If the issuing fluid consists of liquid only—as when the orifice is below the surface of the liquid—then $m_0 = 0$, $v_0 = s_0$, and equations (8) and (9) become

$$\left. \begin{aligned} \frac{v^2}{2} &= f_0 s_0 - f v - m(\lambda - f u) - \int_{t_0}^t \left(s - f \frac{ds}{dt} \right) dt \mp g h \\ \frac{m \lambda}{t} + \int_{t_0}^t \frac{s}{t} dt &= 0, \end{aligned} \right\} \quad (14)$$

the upper or lower sign of the ambiguous term being taken according as the liquid is forced upwards or downwards.

In the case of water very little is vaporized and therefore m may be taken as zero or $v = s$; the temperature is further unchanged (as shewn by the second of the equations) so that $s = s_0$, and therefore

$$\frac{v^2}{2} = (f_0 - f)s_0 \mp gh, \quad (15)$$

the formula we obtained in § 102.

CHAPTER X.

Heat-Engines.

WE shall briefly discuss certain heat-engines and their theory, and refer the student for a complete account of them to Professor Rankine's 'Manual of the Steam-Engine and other Prime Movers.'

105. M. Carnot's engine. We have described this fully in § 35: we will now merely find the changes of volume during the operations on the supposition that the working substance is a perfect gas. Denoting A (fig. 11) by p_0, v_0 , B by p, v , C by p', v' , D by p'_0, v'_0 , the isothermals BC, AD being for the temperatures t, t_0 respectively, we have by (62), § 63, since AB, CD are adiabatics,

$$\left(\frac{v_0}{v}\right)^{\kappa-1} = \frac{t}{t_0} = \left(\frac{v'_0}{v'}\right)^{\kappa-1},$$

and therefore

$$\frac{v_0}{v} = \frac{v'_0}{v'} \quad \text{or} \quad \frac{v'}{v} = \frac{v'_0}{v_0} \quad (1)$$

and therefore also

$$\frac{p}{p'} = \frac{p_0}{p'_0} \quad \text{or} \quad \frac{p}{p_0} = \frac{p'}{p'_0} \quad (2)$$

Further the areas $BAabB, CDdcC$ are equal, being each equal to $\frac{R}{\kappa-1}(t-t_0)$ by (64), § 63: also the area $BCc\delta B$, which represents the heat H given by the boiler—since the isenergetics and isothermals of a perfect gas coincide—is

$$R t \log_e \frac{v'}{v};$$

similarly the heat h given out to the refrigerator is

$$R t_0 \log_e \frac{v'_0}{v_0},$$

whence the efficiency is

$$1 - \frac{t_0}{t} \frac{\log_e \frac{v_0'}{v_0}}{\log_e \frac{v'}{v}} = 1 - \frac{t_0}{t}$$

by the above relation, as we should expect.

106. Engines of maximum efficiency. If t, t_0 are the highest and lowest temperatures between which an engine works, the maximum efficiency attainable by the engine is $\frac{t-t_0}{t}$, as shewn in § 41, and it can only be obtained if heat is taken in only at t and given out only at t_0 , as in M. Carnot's engine. But with air as the working substance this engine is really impracticable by reason of the enormous cylinders that would be required, since the rise in temperature from t_0 to t would have to be obtained entirely by compression and the fall from t to t_0 entirely by expansion: there are however an infinite number of other engines possible which possess maximum efficiency when they work under the following conditions, which are equivalent to M. Carnot's:—(1) that heat is taken in from and given out to external bodies only at two fixed temperatures, (2) that in the passage of the working substance from a higher temperature to a lower during any stroke all the heat is given out that is necessary to bring the substance from the lower temperature to the higher in the next stroke, being in the meantime stored up within the engine itself. Thus, if the cycle performed is $ABCD$, where AD, BC are the isothermals, corresponding to the extreme temperatures at which alone the working substance is in communication with the exterior, and if in passing from Q' to Q the substance emits as much heat as it absorbs in passing from P to $P', PQ, P'Q'$ being any pair of isothermals, the engine will have maximum efficiency. The part of the engine

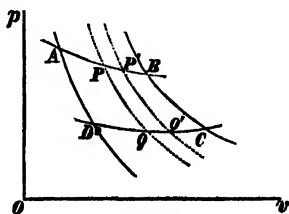


Fig. 48.

wherein heat is stored between successive strokes of the piston is called the *economiser* or *regenerator*, and its invention is due to Dr. Stirling: in its latest form it consists of a chamber containing thin plates of metal or other solid conductors or a network of wires; these become heated as they cool the fluid passing through them, and restore the heat when the cooled fluid repasses in the contrary direction. Practically this process is not perfect, as heat is lost by conduction, &c.; but the waste can be reduced below five per cent. of the heat alternately abstracted from and restored to the fluid.

We can easily determine the relation between the curves AB and CD so that $ABCD A$ shall be a cycle of maximum efficiency. If the equation of AB be $p = F(v)$, we may eliminate v between this and the characteristic equation of the working substance of the engine $f(p, v, t) = 0$ and express the result as

$$p = \chi(t), \quad (3)$$

and corresponding to CD we shall get a similar equation

$$p' = \psi(t).$$

Now if $PQ, P'Q'$ are consecutive isothermals, unit-mass of the substance will absorb $K dt + L dp$ heat in passing from P to P' and give out $K dt + L' dp'$ in passing from Q' to Q ; these quantities are to be equal, and we therefore have, by (8), § 53,

$$\frac{\partial v}{\partial t} dp = \frac{\partial v'}{\partial t} dp'.$$

For working substance we may use a perfect gas, for which $p v = R t$, and the equation becomes

$$\frac{dp}{p} = \frac{dp'}{p'},$$

whence

$$p = c p', \quad (4)$$

c being a constant; and this is the relation that must subsist between the pressures at the points P, Q where the paths AB, CD cut any isothermal. Professor Rankine calls two such lines as AB, CD *isodiabatic* to each other.

107. Dr. Stirling's engine. In this case (3) is $p = at$, where a is a constant, so that if air is used in the engine $v = \text{const.}$ is the equation to the lines AB, CD , or they are isometrics. The air thus (1) is raised in the regenerator from

t_0 to t at constant volume, (2) expands at this constant temperature on receiving heat from the furnace, (3) is cooled to t_0 in passing through the regenerator at constant volume, (4) contracts at this constant temperature, giving up heat to the refrigerator.

In this engine, invented in 1816, the air is enclosed in a receiver *DCABACD*, consisting of two similar vessels one within the other, which communicate by holes pierced through the hemispherical bottom of the inner one; the annular space *AC* between them containing conducting materials and forming the regenerator. A plunger *E*, which is hollow and filled with brick-dust or other badly-conducting matter, moves up and down within the internal vessel, and by driving or drawing the air through the regenerator causes it to be cooled or heated at constant volume: the refrigerator consists of a fine copper tube coiled horizontally in the space *CD* and traversed by a current of cold water: *G* is the cylinder and *H* the working piston. Consider the plunger at the bottom of its stroke; as it rises, the cold air passes from above through the regenerator and through the holes into the space vacated, being thus heated at constant volume; receiving heat from the furnace on which the receiver stands the air expands at constant temperature, lifting the piston *H*; as the plunger descends, the air passes through the regenerator, leaving its heat there and being cooled at constant volume, and then through the refrigerator to the vacated space, being thus brought to its lowest temperature; the refrigerator absorbs also the heat produced by the compression of the air in *G* as *H* descends. A slide-valve is required for this engine which is not shewn in the figure.

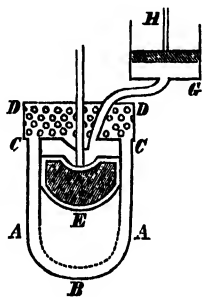


Fig. 49.

108. Captain Ericsson's engine. In this cycle (3) is $p = \text{const.}$, or the lines *AB*, *CD* are isopiestic. The air therefore (1) passes through the regenerator at constant pressure, being heated from t_0 to t , (2) receives heat from the furnace

and expands at this constant temperature, (3) repasses the regenerator at constant pressure, falling again to t_0 , (4) is compressed at this constant temperature, giving up heat to the refrigerator.

This engine was invented¹ in 1833, and it was much improved by Mr. Duna² in 1850. In the improved form it consists of a cylinder A into which air is drawn through the valve f as the piston a descends: when the piston rises, the air is chased through the valve g into the receiver D , whence it passes at constant pressure through the regenerator E , where

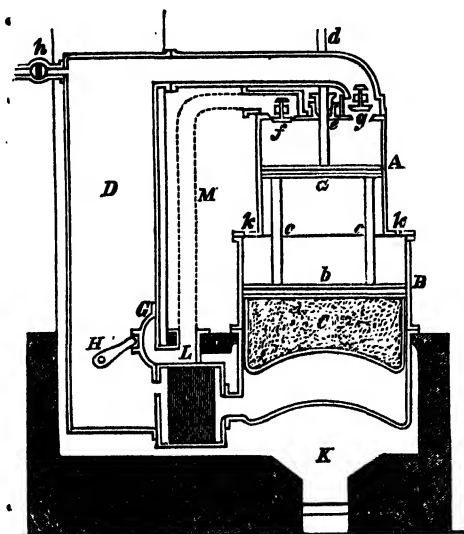


Fig. 50.

its temperature is raised to t_1 into the cylinder B : here it is heated by the furnace K and raises the piston C , which is hollow and full of brick-dust, and which is connected to the piston a by the braces c ; as C descends, the air passes out through the regenerator, giving up its heat, and is caused by the slide-valve G (which is moved by the eccentric H) to go into the

¹ *Mechanic's Magazine*, xx. (1833) 11.

² *Mechanic's Magazine*, lv. (1851) 41.

waste-pipe L communicating with the atmosphere. If any other gas than air is used, it is passed by L through the tube M , around which is a refrigerator, to the valve f , where it again enters the engine. k, k are air-holes, and e the stuffing-box of the piston-rod d .

109. Dr. Joule's engine. In 1851 Dr. Joule¹ proposed an engine without regenerator or refrigerator, which though not theoretically of maximum efficiency approaches this limit more nearly in practice than the theoretically perfect engines: its diagram consists of isopiestic and adiabatics. Air is drawn from the atmosphere into a cylinder, its state being represented by p_0, v_0, t_0 ; it is then compressed adiabatically till its state becomes p, v, t , and is then forced into an indefinitely large reservoir containing air that is kept constantly at a high temperature t' and at the pressure p by a furnace: here it absorbs heat $K(t' - t)$ per unit-mass as it rises in temperature to t' , meantime expanding at the constant pressure p into a cylinder and driving a piston before it: when as much air has left the reservoir as entered it, communication with the reservoir is shut off and the air in the cylinder is allowed to expand adiabatically till its pressure falls to its initial value, it is then rejected into the air as the engine returns to its initial state, the piston in this last process experiencing a back pressure p_0 .

We have then

$$A(p_0, v_0, t_0), \quad B(p, v, t),$$

$$C(p, v', t'), \quad D(p_0, v'_0, t'_0);$$

and between these quantities the properties of adiabatics and isopiestic give the relations

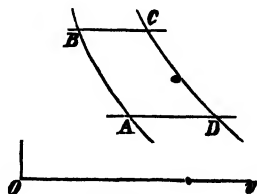


Fig. 51.

$$\left(\frac{v_0}{v}\right)^{\kappa} = \left(\frac{t}{t_0}\right)^{\frac{\kappa}{\kappa-1}} = \frac{p}{p_0} = \left(\frac{t'}{t_0}\right)^{\frac{\kappa}{\kappa-1}} = \left(\frac{v'_0}{v'}\right)^{\kappa};$$

$$\frac{v'_0}{v} = \frac{t'}{t}, \quad \frac{v'_0}{v_0} = \frac{t'_0}{t_0};$$

¹ *Phil. Trans.* cxlii. (1852) pt. i. 65.

thus the work done along BC is $p(v' - v) = R(t' - t)$, the work done along CD is $k(t' - t_0) = k \frac{t'}{t} (t - t_0)$, the work spent along DA is $p_0(v'_0 - v_0) = R(t'_0 - t_0) = R \frac{t'_0}{t} (t' - t)$, the work spent along AB is $k(t - t_0)$; hence the total work done is

$$K(t' - t) \frac{t - t_0}{t}, \text{ since } K - k = R,$$

and the efficiency is therefore

$$1 - \frac{t_0}{t} \quad \text{or} \quad 1 - \frac{t'_0}{t'},$$

which is not the maximum.

110. Steam-engine. We shall consider a theoretical steam-engine in which none of the irreversible processes that occur in practice are found. Thus, in the diagram unit-mass of water

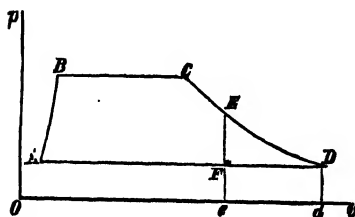


Fig. 52.

at t_0 , the temperature of the condenser, is heated to t , the temperature of the boiler, under a pressure which is at each instant equal to the maximum tension of steam at the corresponding temperature; it is then vaporized at t and expands

into a cylinder the piston of which it drives out; it is then allowed still further to expand adiabatically until its temperature falls to t_0 ; it is finally put in communication with the condenser and compressed till it regains its original liquid state.

The heat given is $\int_{t_0}^t s dt$ along AB and λ along BC ; now a proportion $1 - m_0$ of the steam will have been condensed during the adiabatic expansion along CD so that the heat given out along DA is $m_0 \lambda_0$, which is given by

$$\frac{\lambda}{t} - \frac{m_0 \lambda_0}{t_0} + \int_{t_0}^t \frac{s}{t} dt = 0$$

from (18), § 88; hence the total work done is

$$\int_{t_0}^t s dt + \lambda - m_0 \lambda_0 = \int_{t_0}^t \frac{t-t_0}{t} s dt + \lambda \frac{t-t_0}{t},$$

and the efficiency is this quantity divided by

$$\int_{t_0}^t s dt + \lambda.$$

If the temperatures of the boiler and condenser are 150° and 50° C., so that $t = 423.7$, $t_0 = 323.7$, giving a maximum efficiency of 0.236, we find, on calculating from the table in § 93, $m_0 = 0.824$, $m_0 \lambda_0 = 19562$, $\int_{t_0}^t s dt + \lambda = 25009$; whence the efficiency is 0.218, or $\frac{1}{3}$ ths of the maximum.

In the actual engine we cannot allow the complete expansion denoted by CD because of the very large values of s' : thus with the temperatures 150° and 50° C., D corresponds to a volume 26.14 times greater than the volume at C , whereas in practice a four-fold expansion (which lowers the temperature to $99\frac{1}{3}^\circ$ C.) is ordinarily employed, the most extreme case being a ten-fold expansion which lowers the temperature to 72.9° C. Thus if the adiabatic expansion CE only is allowed and the steam is then put into communication with the condenser, the work $EDFE$ is lost, and this may be thus calculated. If t_1 is the temperature at E , the area $EDdeE$ is

$$m_1(\lambda_1 - f_1 u_1) - m_0(\lambda_0 - f_0 u_0) + \int_{t_0}^{t_1} (s - f \frac{ds}{dt}) dt,$$

by (14), § 86, and the area $FDdeF$ is

$$f_0(v_0 - v_1) = f_0(m_0 u_0 + s_0 - m_1 u_1 - s_1);$$

but at the same time we have

$$\frac{\lambda}{t} - \frac{m_1 \lambda_1}{t_1} + \int_{t_1}^t \frac{s}{t} dt = 0;$$

and the work $EDFE$ is equal to the excess of $EDdeE$ over $FDdeF$.

If in the above case we allow a four-fold expansion, $m_1 = 0.911$, $m_1 \lambda_1 = 20308$, area $EDdeE = 2539$, area $FDdeF = 1041$, whence the area $EDFE = 1498$, and the efficiency of the engine

is diminished by 0.060, being therefore only $\frac{2}{3}$ ths of the maximum. Had the adiabatic expansion been ten-fold, the efficiency would have been diminished by 0.022 and therefore $\frac{1}{5}$ ths of the maximum.

We ought further to allow for clearance (the space within the cylinder that is not traversed by the piston, including also the ports) and for the steam reaching the cylinder at a temperature lower than that of the boiler: for these details however we must refer to Professor Rankine's book.

Another imperfection of an ordinary steam-engine arises from the condensation of steam during expansion; the heat thus emitted certainly does work, but at the same time it turns the badly-conducting saturated but dry vapour into a fairly-conducting mixture of steam and water, so that the condensed particles, abstracting heat from the entering steam and communicating heat to the cooled steam as it leaves the cylinder, lowers the working pressure and increases the back pressure, thereby seriously affecting the efficiency of the engine. Mr. Watt remedied this by enveloping the cylinder in an annular casing, called a *steam-jacket*, which communicates with the boiler, and thus being filled with steam supplies sufficient heat to prevent condensation within the cylinder.

We may apply Fig. 52 to this case, the only difference being that the same ordinates of CD correspond to greater abscissæ than in the ordinary engine. Considering the full expansion to occur, we have heat $\int_t^{t_0} s' dt$ added along CD , so that the heat supplied is

$$\begin{aligned} \int_{t_0}^t s dt + \lambda + \int_t^{t_0} s' dt &= \lambda + \int_{t_0}^t \left(\frac{\lambda}{t} - \frac{d\lambda}{dt} \right) dt \\ &= \lambda_0 + \int_{t_0}^t \frac{\lambda}{t} dt, \end{aligned}$$

by (8), § 83, and as λ_0 is the heat emitted along DA , the heat turned into useful work is

$$\int_{t_0}^t \frac{\lambda}{t} dt.$$

If the temperatures of the boiler and refrigerator are 150°

and 50°C. , we find 6011 for the value of the integral or the work done during the stroke, and the efficiency is therefore 0.202 or $\frac{2}{9}$ ths of the maximum. This is less than that given by the ordinary engine; at the same time 563 megalergs more work is done per stroke, but only by absorbing 4747 megalergs more of heat and by expanding $\frac{1}{3}$ th as much again. A steam-jacket is thus no improvement to an engine so perfect as we have supposed: it is found however practically to be of great advantage in the case of actual steam-engines.

We might easily apply this to the case of partial expansion until the temperature falls to t_1 as denoted by E ; the heat supplied is

$$\int_{t_0}^t s dt + \lambda + \int_t^{t_1} s' dt = \lambda_1 + \int_{t_0}^{t_1} s dt + \int_{t_1}^t \frac{\lambda}{t} dt;$$

and the work $EDdeE$ is equal to the excess of the heat supplied along ED over the change of intrinsic energy, or

$$\begin{aligned} \int_{t_1}^{t_0} s' dt - \{(\lambda_0 - f_0 u_0) - (\lambda_1 - f_1 u_1) + \int_{t_1}^{t_0} (s - f \frac{ds}{dt}) dt\} \\ = \int_{t_0}^{t_1} \frac{\lambda}{t} dt + f_0 u_0 - f_1 u_1 - \int_{t_0}^{t_1} f \frac{ds}{dt} dt, \end{aligned}$$

and the work $FDdeF$ is $f_0(v_0 - v_1)$, and the lost work $EDFE$ is the difference between these quantities: the efficiency may therefore be calculated.

If in the above case a four-fold expansion were allowed, the vapour would be cooled to 102°C. : thus the heat supplied would be 27948, the area $EDdeE$ 3201, and the area $FDdeF$ 1285, so that the area $EDFE$ would be 1916 and the total work done 4095, whence the efficiency is 0.147 or $\frac{9}{60}$ ths of the maximum.

Other engines have been employed with superheated vapours and with combined vapours: these are fully discussed by Professor Rankine.

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